

Section 7. Monitoring Methods and Issues

7.1 Background/Introduction

The Strategy goal is to manage the Nation's air monitoring networks such that critical and stable network elements, as well as changing priorities, can be accommodated in a framework that is scientifically sound and resource-optimized to address national and local interests. This framework requires progress on various aspects that shape the monitoring networks, including the incorporation of emerging technological and scientific advances in measurement techniques to support these monitoring efforts. Several different measurement techniques are needed to support the existing monitoring program efforts. The list of measurements provided in Section 4 includes mostly those that are required with some recommendation on additional measurements.

The information in this section supports the overall Strategy approach by providing a general understanding of (and issues related to) routine monitoring and new technologies currently available to provide the measurements outlined in the Strategy. Its goal is to help provide insight for those deciding how these measurements will be obtained. An attempt is made to strike a balance between the routine, easy-to-use, “tried and true” and the new, commercially available, continuous, and not-yet-fully-demonstrated technologies. Recognizing that other techniques may be applicable to the measurements discussed, the methods provided here are those used in current EPA monitoring networks. This discussion does not include PM mass and PM continuous measurements.

It is important to distinguish between “routine” and “non-routine” methods for monitoring. Routine methods are thought to be fully field demonstrated, tested and routinely used in networks such as the National Ambient Air Quality Standard (NAAQS) networks. Routine methods are those that are usually simple to implement, use and maintain, stable in operation and do not require significant resources to operate. Non-routine methods are considered less “rote,” more research-oriented, more difficult to maintain, and require a specially trained or skilled operator. Non-routine methods may also be new technologies that have not yet been fully field tested or evaluated.

In keeping with the goal of providing insight to those implementing monitoring methods, this section is an overview of the methodologies, and a synopsis, of what is considered to be currently “working” and what is not. This section touches on the key issues with each of the methods and is grouped by program. It is not in any order of priority. To address an overview of measurement method operating principles for gas-phase species that are relevant to secondary PM formation, refer to **Attachment 7.1** as excerpted from Seigneur et. al., 1998. The overview of operating principles for the remaining species is included here.

7.2 Criteria Pollutants (CO, SO₂, NO₂, O₃)

Federal Reference Methods (FRMs) and Equivalent Methods (FEMs) used for criteria pollutants were developed by the Office of Research and Development (ORD) and are explicitly defined in the Federal Register. The methods for the criteria pollutants (except PM and lead are not addressed here) are working well for NAAQS decision-making purposes. In considering these methods for other applications, such as measurements in rural areas or for more research-oriented applications, technical issues and limitations have been identified. In addition, as these methods have been implemented and operated under rigorous field conditions, over time issues have been uncovered. In some cases, the issues are inherent limitations in the technique being applied and in other cases the issues are difficult to resolve because they are not reproducible.

When applied to situations where very low concentrations need to be measured (e.g., rural monitoring), issues with measurement sensitivity exist for the CO and SO₂ methods. Manufacturers of NDIR (non-dispersive infrared) CO monitors are continuing to improve the performance and offering “high-sensitivity” options, like the TECO 48C trace-level analyzer, that allow for detection limits around 0.10 ppbv. The principal constraints on the ability to lower detection limits further are detector noise, interference from water vapor and background drift. These issues can be addressed by drying the sample stream, frequent zero and span checks (e.g., every 90 seconds), and active temperature control of the optical bench and instrument cabinet. This requires a significant amount of post-data processing that may be burdensome for some.

Similar issues with sensitivity for rural or background applications apply to automated methods for SO₂. High-sensitivity options of the pulsed-UV fluorescence continuous monitoring technique (e.g., TECO 43C trace-level analyzer) provide lower detection limits on the order of 0.10 ppb for 60 second averaging times. SO₂ monitors are affected by temperature and water vapor. The temperature affect is not as great as with CO monitors; therefore, no on-board temperature control is necessary. These limitations can be addressed by frequent zero and span checks. A NO_x interference exists. There is a NO_x rejection ratio of 40-50:1, where 40-50 ppb NO_x results in a 1 ppb SO₂ instrument response.

Oxides of nitrogen, NO_x (NO₂ + NO) measurements using chemiluminescence do not determine NO₂ directly. NO is determined directly and NO₂ is determined by the difference between the measured total NO_x value and the corresponding measured NO. Chemical reductant and heated metal converters are not specific for NO₂ and convert all nitrogen species present in the atmosphere to NO. This presents a positive bias in the measurement of NO_x and consequently NO₂. As such, these instruments serve as better NO_y monitoring devices in rural areas than NO₂ monitoring devices because of the non-specific conversion of nitrogen species. Sensitivity of the instruments is adequate (as low as 2 ppbv) for rural applications, but a “direct or true” NO₂ measurement is needed. A photolytic converter can provide improved accuracy in determining both NO_x and NO₂. EPA-ORD is currently evaluating instruments that can be used in conjunction with

the current NO_x monitors and complete stand-alone photolytic systems. Photolytic system detection limits are on the order of 3 ppt. Diode lasers now available in photolytic converters are another alternative being evaluated by ORD.

Measuring NO_y is a valuable adjunct to NO and NO_x monitoring because the individual species comprising NO_y include not only NO and NO₂, but also other organic and inorganic nitrogen oxide compounds that constitute a more complete measure of nitrogen oxides emissions. In typical urban environments, the principal NO_y compounds are NO, NO₂, HNO₃, and PAN. Determining NO_y concentrations is useful in establishing nitrogen oxide emission patterns and temporal trends, and in assessing the photochemical “age” and reactivity of air masses. Guidance on measuring NO_y, including measurement principles, calibration procedures, and equipment descriptions, have been prepared for the PAMS program. It is not possible to individually measure all the compounds that comprise ambient NO_y. Measuring several key NO_y constituents is expensive and technically difficult. However, the chemiluminescence monitoring approach for NO and NO_x described above is a practical approach to determining the total NO_y level, once the converter has been moved as close to the inlet as possible. For consistency in measurements, NO_y should be measured in a practical and standardized manner. Instruments used to measure NO_y should be sensitive enough to measure the low concentrations typically encountered during the late afternoon as well as the high concentrations encountered during the early morning hours of the day. Automatic measurement range changing will more reliably accommodate the range of NO_y concentrations experienced in a typical urban atmosphere. It is recognized that NO_y measurement is an emerging technology and as advances in the technology are made, the methods should be updated.

Chemiluminescence is the FRM for ozone; however, the most popular technique for ozone has been UV photometry because of simplicity and ease of use. UV ozone monitors are susceptible to interferences by aromatic hydrocarbons, water vapor and mercury. Whether water vapor truly presents an interference is still under debate. Erratic readings and sometimes cycling monitor baseline readings have been identified by a few state agencies, but the cause of these anomalies has yet to be reproduced or positively identified. Theories have revolved around the specific type of ozone scrubbing device used in the monitor (MgO) and proper scrubber performance is critical to minimizing interferences. Where high levels of potential interferences are expected, the use of chemiluminescence monitors are recommended; however, commercial availability of these monitors is limited.

7.3 PM_{2.5} Chemical Speciation

The most challenging measurement component in the speciation program is carbon, for both the carbonaceous aerosols (organic and elemental carbon) and semi-volatile organic aerosols or organic PM. The analysis of organic (OC) and elemental carbon (EC) is operationally-based and dependent on the purpose of measurement and the specific analytical technique used. Currently, there are no reference standards for

carbon or a standardized method for distinguishing between organic and elemental carbon; therefore, differing results are obtained for the same sample depending on the analytical method operating parameters used. The sampling of carbon is not without issue. Positive and negative sampling artifacts complicate sampling and add a large degree of variability and uncertainty into the measurement. The issues on artifacts are captured in the discussion of organic PM below.

Due to the number of organic compounds present, characterization analysis of the organic chemical composition of PM_{2.5} presents a difficult challenge. The collection of particulate organic matter can be accomplished using particulate sampling instruments equipped with quartz fiber or Teflon®-impregnated glass fiber filters and denuders. This methodology is susceptible to negative (i.e., desorption of semi-volatile compounds from the particles on the filters) and positive (i.e., adsorption of gases by the filter material and particles collected) artifacts. Positive and negative artifacts are of most concern, but there is disagreement as to the cause and extent to which they bias organic PM measurements. The positive artifact is currently thought to be the largest of the two artifacts. The use of denuders is controversial. Stripping of gases upstream of the sampling filter by denuders may disturb the gas-particle equilibrium of the organics, providing a driving force for volatilization. Thus, volatile losses from a filter downstream of a denuder may be greater than the volatile losses experienced by an undenuded filter. Research continues on the development of a denuder that has adequate efficiency and is practical to use.

Once collected, characterization analysis of organic chemical composition requires the analysis of numerous calibration standard mixtures. This is needed to cover the range of compounds that may be of interest as a result of the hundreds of organic compounds associated with both the gas and particle phases in the atmosphere. The availability and cost of acquiring and synthesizing these analytical standards is problematic.

X-ray fluorescence (XRF) is currently used to obtain data for elemental composition of PM_{2.5}. There are limitations of XRF for the determination of beryllium and the sensitivity of the method (e.g., detection limits) for certain applications. If the application requires quantification of beryllium or greater sensitivity, then consideration should be given to the use of ICP-MS (i.e., inductively coupled plasma - mass spectrometry) as a viable alternative. Comparisons of data obtained by both XRF and ICP-MS have shown the sensitivity of ICP-MS to be an improvement over XRF for some elements. However, ICP-MS is not a panacea. There are some cases where sensitivity of ICP-MS is not as good as XRF (e.g., calcium and potassium). Clearly, more comparison work on PM_{2.5} samples is needed to determine the benefits of XRF and ICP-MS. XRF is non-destructive and typically places the filters under vacuum which may cause volatile compounds to evaporate. As a result, species that can volatilize, such as ammonium nitrate and certain organic compounds, can be lost during the analysis. The effects of this volatilization are important if the filter is to be subjected to subsequent analyses of volatile species. In the PM_{2.5} speciation program, the XRF filter is not used to quantify

volatile species. ICP-MS is a destructive technique and once filters are subject to analysis no repeat analyses can occur.

7.4 Continuous PM_{2.5} Speciation Instruments

Commercial instruments are currently available to measure carbon (OC, EC, TC), nitrate and sulfate. These instruments provide time-resolved measurements from a few minutes to a few hours. They have been field tested and inter-compared through the ETV (Environmental Testing and Verification) program and the Supersites program, and considered to be good candidates for additional testing. Very limited data are available to completely understand the comparison with filter-based methods and the inherent limitations of these technologies. More comparison data are available for the carbon instruments (Aethalometer and R&P5400) as opposed to the nitrate and sulfate instruments. Good correlation with filter-based methods has been found for the R&P5400, but the measurement is biased low. Nitrate, sulfate and carbon continuous instruments will be tested through the EPA's speciation program where they will be run in conjunction with the standard filter-based methods.

The aethalometer has undergone much more extensive inter-comparison testing and has shown very good correlation of BC with EC in a number of studies. Agreement with filter-based methods is highly variable across studies and may be due to the specific attenuation used by the instrument to determine BC. This value can be modified by the user. The aethalometer requires very little maintenance, has on-board data acquisition and can perform for long periods of time without operator involvement.

A continuous PAH (polycyclic aromatic hydrocarbon) monitor is available (EcoChem PAS 2000). Very limited inter-comparison data were collected through ETV due to the very low concentrations of ambient PAH during the test period. The monitor was rated very easy to operate and provides a total PAH measurement only. It is somewhat sensitive to temperature, and requires a "shield" from sunlight. Clearly more field and comparison testing is needed.

7.5 Hazardous Air Pollutants (HAPs) or Toxics

Standardized methods for HAPs are being used in the EPA's Urban Air Toxics Monitoring Program (UATMP) and Air Toxics Pilot Monitoring Network. Most of these methods for VOCs, metals, and carbonyls are adequate for the data collection needs; however, due to the push to leverage existing methods to cover as many of the key HAPs as possible, there are some that cannot be covered by the existing methods used for these programs. Examples include acrolein and ethylene oxide. There are methods for these compounds, but it would require added burden be placed on state agencies to add two more methods to the suite they already have. There are also a few HAPs for which no methods are available (e.g., hydrazine and quinoline). Acrolein is considered a critical HAP from the standpoint of risk, and is not stable using dinitrophenylhydrazine (DNPH)-coated cartridges and Method TO-11a. Because of its importance, ORD, consultants, and some state agencies have done some work to develop methods for acrolein. This work

includes the possible use of Method TO-15 for VOCs and stainless steel canisters; modification of the existing DNPH Method TO-11a; and a method that uses dansylhydrazine-coated C18 cartridges (developed at Rutgers). In addition to total chromium measurements, chromium species (e.g., Cr III and Cr VI) are of interest. CARB has developed a method for Cr VI that has been used by the EPA in emergency response applications. A modification of the CARB method is currently being used by the EPA contractor for the UATM program.

As data from the pilot monitoring network is analyzed, the need for enhanced method sensitivity to meet risk-based concentration requirements may be needed. Sensitivity of the standard methods for one-in-a-million risk-based concentrations would require additional method development for many of the target compounds, especially the chlorinated VOCs. This issue will need to be further evaluated as the pilot network data are analyzed and the program DQOs are developed.

Automated and continuous instruments are commercially available for formaldehyde and speciated gas-phase mercury. Continuous formaldehyde instruments have recently become commercially available in the U.S. at a cost of about \$27K (e.g., Alpha-Omega PT). There is also at least one other vendor of instruments of a similar type in Germany (Aero Laser), and the cost is about \$38K. The U.S. monitor uses a wet chemical technique that poses some issues with operation and maintenance. Regular maintenance includes filling the liquid reservoirs and replacing pump tubing weekly. The monitor is also susceptible to formation of leaks and bubbles which interfere with data collection. The monitor requires a substantial supply of zero air and is most practically supported by a zero air compressor system or zero air generator. Gas calibration can be done using either a gas cylinder of formaldehyde or a permeation tube device. Liquid calibration can also be done using solutions of formaldehyde; however, liquid calibration does not check the inlet and the formaldehyde-scrubbing device. Inter-comparison testing of a prototype monitor during the 1999 Nashville SOS showed good comparison (14 % difference) with a Tunable Diode Laser Absorption Spectrometer (TDLAS) when analyzing a formaldehyde audit cylinder. These monitors require more testing in routine field applications by state agencies to get a better feel for complexity of operation and data recovery. The units are very promising, but somewhat complex to operate and maintain.

A continuous mercury monitor is available (Tekran) that provides both total mercury and speciated or reactive gaseous mercury (RGM) measurements. This instrument has been used extensively by ORD in Florida and other parts of the country. It is recommended that particulate mercury be collected in conjunction with gaseous elemental and RGM to provide a complete picture of the atmospheric behavior of mercury for modeling and emission inventories purposes. Continuous mercury monitors for total and RGM are expensive (~\$95K). An RGM artifact formation on quartz filters collected for particulate mercury has been identified which is resolved through the use of the KCl- coated annular denuder before the quartz filter.

Attachment 7.1

Measurement Methods



GUIDANCE FOR THE PERFORMANCE EVALUATION OF THREE-DIMENSIONAL AIR QUALITY MODELING SYSTEMS FOR PARTICULATE MATTER AND VISIBILITY

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A.1 Measurements of Precursor and Oxidant Gases

This appendix describes measurement methods for gas-phase species that are relevant to secondary PM formation, either directly as precursor species (e.g., NO, NO₂, HNO₃, NH₃), or as gas-phase species that act as oxidants in air, for example those that oxidize NO to NO₂ to HNO₃. Several species partition between the gas and particle phases depending on, for example, temperature and relative humidity. For these species, measurements that strictly measure the gas-phase components, typically continuously, are described in this section. Methods that can simultaneously measure the gas and PM components are described in Section A.2. These methods typically are time-integrated measurements over a few hours to a full day.

Table A-1 summarizes the principal methods used to measure precursor and oxidant gases. The measurement methods are described below by chemical or group of chemicals.

A.1.1 Nitrogen-Containing Species

Methods for the measurement of gas-phase nitrogen species have been reviewed recently by Solomon (1994a) and Parrish and Fehsenfeld (1998). Species included in the reviews are nitric oxide (NO), nitrogen dioxide (NO₂), peroxyacetyl nitrate (PAN), other peroxy nitrates, organic nitrates, nitrate radical (NO₃), nitric acid (HNO₃), and total reactive nitrogen oxides (NO_y). The two reviews differed in their approach. Solomon (1994a) reviewed methods available in 1990 for the purpose of recommending methods for use in the 1990 San Joaquin Valley Air Quality Study (SJVAQS) field program. Thus, Solomon attempted to provide practical information for decisions regarding which instrument to use in the field, stressing analytical capabilities and pros and cons of the methods, including, for example, cost, reliability in the field, and availability. Discussions also included examining results from methods comparison studies for measurements at the surface and aloft. It was updated prior to publication in 1994. Parrish and Fehsenfeld (1998) performed a critical review of current methods, stressing mostly recent developments and methods suitable at very low concentrations, and

Table A-1. Measurements of Precursor and Oxidant Gases

Method	Variable Measured	Limit of Detection (3 σ)/Avg. Time	Precision (1 σ)	Overall Accuracy	Potential Interferences/Artifacts	References
Chemiluminescence						
With O ₃ to NO ₂ *	NO	15 pptv/1s	5%	$\pm 15\%$	--	Fahey et al., 1986
Photolysis to NO	NO ₂	30 pptv/1s	5%	$\pm 30\%$	Conversion of NO _y	“
Reduction to NO	NO _y	60 pptv/1s	5%	$\pm 15\%$	NH ₃ , HCN	“
Luminol	NO ₂	100 pptv/30s	5%	$\pm 10\%$	O ₃ , PAN	Fehsenfeld et al., 1990
with NO to NO ₂ *	O ₃				--	Parrish et al., 1998
with ethylene	O ₃				water vapor	“
Eosin-Y	O ₃	1 ppbv/4s	0.8 ppb at 0 ppbv O ₃		SO ₂ (8% at 300 ppbv SO ₂)	Topham et al., 1990; Topham et al., 1992
Chemical Amplifier	HO ₂ , RO ₂	6 pptv/1m	--	$\pm 100\%$	PAN, PNA, H ₂ O ₂ , O ₃ , variable chain length	Cantrell et al., 1993 Hastie et al., 1991
Gas Chromatography – FID or Mass Spectroscopy	VOC	10 pptv/45m	3% @ 1ppb	$\pm 18\%$	--	Goldstein et al., 1996
NSIS or TDLAS	CO	1 ppm, 0.25 ppb	10%, 4%		--	Fried et al., 1991
Gas Chromatography – Luminol	PAN	25 pptv/30 m		$\pm 25\%$		Blanchard et al., 1990
GC-FID, GC-MS	alkyl nitrates					
Chemical Ionization Mass Spectrometry	OH				inlet surface loss	Tanner et al., 1997
	HNO ₃	13 pptv/1s	10%	$\pm 35\%$	reactor surface effects	Huey et al., 1998
	HO ₂ , RO ₂		20% @20 ppt	$\pm 45\%$	calibration uncertainties	Reiner et al., 1997
Matrix isolation-ESR	HO ₂ , RO ₂ NO ₃	2 pptv 1 pptv				Mihelcic et al., 1993

Table A-1. Measurements of Precursor and Oxidant Gases (continued)

Method	Variable Measured	Limit of Detection (3 σ)/Avg. Time	Precision (1 σ)	Overall Accuracy	Potential Interferences/Artifacts	References
Differential optical absorption spectroscopy	NO ₃	2 ppt/10 m	--	--	water vapor	Carslaw et al., 1997
	NO ₂	4 ppb/12 m	--	$\pm 15\%$	--	Biermann et al., 1988
	HONO	ppb/12 m	--	$\pm 30\%$	--	"
	OH	0.02 ppt/2 m	1% @ 0.2 ppm	$\pm 25\%$	none	Mount, 1992
	SO ₂	20 ppt/10 m	--	--		Platt, 1994
	CH ₂ O	400 ppt/10 m	--	--		"
	O ₃	4 ppb/10 m	--	--		"
Fourier transform infrared spectroscopy	CH ₄	(ambient)/1 m	0.2% @ 2 ppm	$\pm 5\%$	none	Galle et al., 1994
	HNO ₃	4 ppb/15 m	--	$\pm 10\%$	none	Biermann et al., 1988
	VOC	1 to 100 ppb	--	--	spectral congestion	Hanst and Hanst, 1994
Tunable diode laser absorption spectroscopy	NO	1 ppb/1s	5% @ 10 ppb	$\pm 15\%$	optical fringes, thermal drifts, laser mode impurity, laser mode drifts	Pun, 1998
	NO ₂	0.5 ppb/1s	5% @ 10 ppb	$\pm 15\%$		"
	O ₃	2 ppb/1s	5% @ 10 ppb	$\pm 15\%$	inlet loss, surface memory	"
	HNO ₃	240 ppt/10 m	10% @ 1ppb	$\pm 15\%$	none	Horii et al., 1997
	CH ₄	(ambient)/1s	0.1% @ 2 ppm	$\pm 5\%$	uncertainty in data base	Zahniser et al., 1995
	C ₂ H ₆	300 pptv/1s	10% @ 1ppb	$\pm 20\%$	none	Zahniser et al., 1998
	CH ₂ O	100 ppt/5 m	5% @ 1ppb	$\pm 12\%$	none	Fried et al., 1997
	CO	(ambient)/5s	1% @ 50 ppb	$\pm 1\%$		Sachse et al., 1991
Non-dispersive infrared absorption	CO	(ambient)/1 h	2% @ 200ppb	--	water vapor on catalyst	Parrish et al., 1994
	CO ₂	(ambient)/10 s	0.1%	--	--	--

Table A-1. Measurements of Precursor and Oxidant Gases (continued)

Method	Variable Measured	Limit of Detection (3 σ)/Avg. Time	Precision (1 σ)	Overall Accuracy	Potential Interferences/Artifacts	References
Laser induced fluorescence	OH	0.01 ppt/60s	5-15%	$\pm 16\%$	sensitivity varies with H ₂ O	Hofzumahaus, 1996
	HO ₂	0.005 ppt/30s	30%	$\pm 50\%$	conversion to OH with NO	Stevens et al., 1994
	NO ₂	280 ppt/2.5 m	--	$\pm 15\%$	none at present	Fong et al., 1997
	NO	<5 ppt			--	Bradshaw et al., 1985
UV absorption	O ₃	1 ppbv/ 10 s	--	$\pm 3\%$	none	--
VUV fluorescence	CO	2 ppbv/ 10 s	--	--	--	Haaks, 1998
TTFMS	NO	Low pptv range				Cooper et al., 1994
	NO ₂					
	HNO ₃					
	PAN					
	H ₂ O ₂					

highlighting tests or comparison studies performed to determine instrument reliability. Both reviews provide brief descriptions of the methods. Much of the information described below is summarized from these reviews.

In this report, unless otherwise noted specifically, NO_x refers to the sum of NO + NO_2 + some typically unknown fraction of interfering species (i.e. other nitrogen oxides) rather than just the sum of NO + NO_2 . NO_y refers to the true sum of all gas-phase reactive odd-nitrogen oxide species: NO + NO_2 + HNO_2 + NO_3 + PAN + NO_3 + HONO + $2\text{N}_2\text{O}_5$ + aerosol nitrate + organic nitrates + etc. (Bollinger et al. 1983, Logan 1983, Dickerson 1985, Fahey et al. 1985, Fehsenfeld et al. 1987, Kelly et al. 1989). N_2O_5 is included in the list of odd-nitrogen species because it is in equilibrium with NO_2 and NO_3 .

Nitric Oxide (NO)

Several methods are available for the measurement of nitric oxide in the atmosphere. These include the widely used ozone (O_3)/NO chemiluminescence method and four spectroscopic techniques: tunable diode laser absorption spectroscopy (TDLAS), differential optical absorption spectroscopy (DOAS), two-tone frequency modulated spectroscopy (TTFMS), and laser-induced fluorescence (LIF).

The O_3 /NO chemiluminescence method is widely used for the measurement of NO in the atmosphere. It is based on the chemical reaction of NO with added ozone followed by the detection of radiation emitted by an excited state of the NO_2 formed in the reaction of NO and O_3 (Fontjin et al., 1970; Ridley and Howlett, 1974). The intensity of the reaction is proportional to the concentration when properly calibrated against NO standards of known concentration. Background chemiluminescence, for example, from hydrocarbon species that chemiluminesce slower on reaction with O_3 than NO, can be minimized by the use of a pre-reaction chamber (Ridley and Howlett, 1974; Delany et al., 1982; Dickerson et al., 1984; Drummond et al., 1985; Grosjean and Harrison, 1985; Kley and McFarland, 1980; Kelly, 1986). The pre-reaction chamber also allows for the maintenance of a stable instrument zero if operating properly. Several of the commercially available instruments sold since the early 1990 include a pre-reaction

chamber (e.g., TEI Model 42S and Tecan Envia Model CLD 700 AL). Limits of detection range from about 5 ppb in older, pre 1990 units (e.g., TEI Model 14) to in the range of 0.5 - 1 ppb (e.g., TEI 42), to 0.01-0.50 ppt (e.g., TEI Model 42S). Accuracy and precision are well established for this method and when used in intensive monitoring networks are on the order of about 5-10% depending on the concentration range of interest (Solomon and Thuillier, 1994, p. 5-8 and references cited therein). The O₃/NO chemiluminescence method has been compared to the two-photon LIF method under low NO concentrations. Agreement was within 15-20 ppt and an uncertainty of 5 ppt was noted in the measurement (Gregory et al., 1990a).

TDLAS relies on measuring the absorbance of IR radiation at specific wavelengths due to a single pollutant (Schiff et al., 1983, 1987; Walega et al., 1984; Mackay and Schiff, 1987; Finlayson-Pitts and Pitts, 1986 and references cited therein). A number of chemical species have been measured, including CO, O₃, SO₂, N₂O, NH₃, CH₄, HCl, NO, NO₂, H₂O₂, HCHO, and HNO₃ (Mackay et al., 1988, 1990; Drummond et al., 1989a; Schiff et al., 1990; Fried et al., 1991; Pokrowsky and Herrmann, 1981). The detection limits for NO and other species is about 0.025-0.5 ppb and depends on factors such as integration time and path length that range from 0.1 to 1 km (Schiff et al., 1983; Mackay and Schiff, 1987; Mackay et al., 1988; Fehsenfeld et al., 1990). The TDLAS provides a nearly interference-free measurement of the specific species monitored (Schiff et al., 1983), and therefore, has been considered the reference method in a number of intercomparison studies (Hering et al., 1988; Drummond et al., 1989a; Sickles et al., 1990; Fehsenfeld et al., 1990; Gregory et al., 1990a). The TDLAS requires a skilled operator. Since the TDLAS can be considered a reference method, its use, at least at one site, is strongly recommended for quality assurance/quality control (QA/QC) purposes. However, caution is recommended as the sample is brought into the system through an inlet line and losses or chemical reactions can occur during transport through the inlet line.

DOAS determines atmospheric concentrations in situ by measuring the absorption of the species of interest in the ultraviolet/visible wavelength region. DOAS is based on measuring the difference between the absorbance at a wavelength where the species of interest has a distinct peak, and another wavelength on either side of that peak (Platt et

al., 1980; Winer and Biermann, 1989 and references cited therein; Biermann et al., 1988; Finlayson-Pitts and Pitts, 1986 and references cited therein; Plane and Nien, 1992; Plane and Smith, 1995). High sensitivities are obtained by combining the detector with a long-pathlength, using either natural light (the moon or near-dawn sunlight) or a multiple-reflectance system, the latter of which yields optical pathlengths up to 10 km (Plane and Smith, 1995; Smith et al., 1995; Solomon et al., 1989a, 1989b). Concentrations are determined from the pathlength and from absorption coefficients. Therefore, this is an absolute, highly specific, and nearly interference-free measurement method that can be considered as a reference method (Biermann et al., 1988; Appel et al., 1989; Winer and Biermann, 1989).

DOAS has been used to measure several chemical species in the atmosphere, including NO, NO₂, HONO, NO₃, HCHO, SO₂, O₃, and OH (Biermann et al., 1988; Appel et al., 1990; Winer and Biermann, 1989; Fried et al., 1997). Several species can be monitored simultaneously. The detection limits for NO are around 1 ppb (Plane and Nien, 1992; Plane and Smith, 1995; Finlayson-Pitts and Pitts, 1986). DOAS is commercially available from several vendors.

TTFMS is similar to FTIR in that it is used to determine the concentration of small molecules that have fairly simple absorption spectra in the infrared (e.g., NO, NO₂, HNO₃, PAN, H₂O₂, and others, see Hansen, 1989; Cooper et al., 1994). However, in TTFMS a diode laser is the light source, which is modulated simultaneously at two arbitrary but closely spaced frequencies. The beat tone between these two frequencies is monitored as the laser carrier and associated sidebands are tuned through an absorption line (Hansen, 1989). The TTFMS is highly specific and extremely sensitive, with detection limits for a number of species, including NO, in the ppt range. The measurement cell can either be a low-pressure, multiple-reflection optical cell with pathlengths of 100 m or more, which provides the best sensitivity, or measurements can be made in situ (i.e., at atmospheric pressure) with a long-pathlength, multiple-reflectance system similar to the FTIR. Only research grade instruments are available and no specific information was found regarding accuracy.

LIF relies on the absorption of radiation by NO in the sampled air, followed by the detection of fluorescence from the excited NO (Bradshaw et al., 1985; Sandholm et

al., 1990). A more detailed description of the method for NO, NO₂, and NO_x is given in Sandholm et al. (1990). LIF is sensitive and relatively free from interferences with limits of detection in the low ppt range. Comparisons of chemiluminescence and LIF methods for NO at ground level and aloft from aircraft platforms have shown agreement to within 30% in the concentration range of 5 to 200 ppt (Hoell et al., 1984; Gregory et al., 1990a).

Nitrogen Dioxide (NO₂)

Several methods are available for the measurement of nitrogen dioxide in the atmosphere. These include the O₃/NO chemiluminescence method after reduction of NO₂ to NO, the luminol fluorescence method, and four spectroscopic techniques: tunable diode laser absorption spectroscopy (TDLAS), differential optical absorption spectroscopy (DOAS), two-tone frequency modulated spectroscopy (TTFMS), and laser induced fluorescence (LIF).

The most widely used method for the measurement of NO₂ involves the reduction of NO₂ to NO followed by detection of NO using the O₃/NO chemiluminescence detector (Fontijn, 1970; Ridley and Howlett, 1974) described above. Reduction can be performed at a surface, catalytically or thermally, or photolytically in the gas-phase. Reduction of NO₂ to NO at a surface includes the use of a heated catalyst (molybdenum or gold in the presence of CO) (Dickerson et al., 1984; Fehsenfeld et al., 1987; Fahey et al., 1985) or chemically using FeSO₄ (Winfield and Buffalini, 1977; Stedman et al., 1977; Dickerson, 1984; Ridley et al., 1988a, 1988b). NO₂ concentrations are then determined by difference. The reduction of NO₂ to NO by these methods is not specific and a number of other nitrogen-containing species can interfere with the measurement of NO₂ (e.g., HNO₃, PAN, NH₃, N₂O₅, HONO, and NO₃) resulting in an overestimation of NO₂ by these methods (Winer et al., 1974; Cox, 1974; Grosjean and Harrison, 1985; Bollinger et al., 1983; Dickerson, 1985). Therefore, the thermal catalytic method is used to measure NO, and then NO plus other nitrogen oxides as a group (NO_x or NO_y). If the group is not well defined, it will be referred to in this report as NO_x, since the species included in the group depend on a number of factors, such as inlet and line losses. With the proper design, all gas-phase nitrogen oxide species can be measured and this group is referred to

as NO_y (Bollinger et al., 1983; Logan, 1983; Dickerson, 1985; Fahey et al., 1985; Fehsenfeld et al., 1987; Kelly et al., 1989). The measurement of NO_y is discussed in more detail below.

In the photolytic reduction method, NO₂ is first photolytically reduced to NO using UV radiation, and then measured using the ozone/NO chemiluminescence detector (Kley and McFarland, 1980). Reduction by this method is specific to NO₂ and other oxides of nitrogen do not interfere with the measurement; however, the method is not as simple as surface reduction methods. NO₂ concentrations are then determined by difference. A description of the method and the performance of the photolytic instruments are discussed in detail by Parrish et al. (1990) and Fehsenfeld et al. (1990).

The luminol method (Maeda et al., 1980; Wendel et al., 1983; Schiff et al., 1986; Drummond et al., 1989a, 1989b) measures NO₂ directly by detecting the chemiluminescence produced when NO₂ reacts with a specially formulated solution containing water, luminol, Na₂SO₃, NaOH, and alcohol ("Luminol II" solution) in proportions chosen to enhance the sensitivity and minimize interferences. The signal is proportional to the chemiluminescence from the luminol oxidation. The instrument is very sensitive with a detection limit (2 sigma) of 5 ppt if zeroed every 30 min or 50 ppt if zeroed daily. Fehsenfeld et al. (1990) observed a 5 ppt detection limit using only a 3 sec integration of zero air and 1 ppt for a one minute integration, during an intercomparison study. The response time of the Luminox^R instrument is fast (1 for a 10-ppb step change; Fehsenfeld et al., 1990) relative to the more sensitive chemiluminescence instruments, and along with its high sensitivity, small size, and low power consumption, makes the Luminox^R instrument suitable for NO₂ measurements aloft from aircraft. However, the detector is sensitive to changes in pressure (i.e., changes in altitude) and temperature; but these can be corrected for mathematically if simultaneous pressure and temperature measurements are obtained (Bubacz et al. 1987; Kelly et al. 1990; Drummond, 1989b, 1991). Several groups have used the Luminox^R instrument for sampling NO₂ aloft from aircraft (Kelly et al., 1990; Solomon and Thuillier, 1994).

Known interferences for the measurement of NO₂ by the luminol method are O₃ (1% or less of the O₃ concentration, measured as NO₂) and PAN (0-70% of the PAN concentration measured, as NO₂) (Sacco, 1989; Wright et al., 1989; Kelly et al., 1990;

Fehsenfeld et al., 1990). These interferences can become significant at NO₂ levels below 1-2 ppb (Drummond et al., 1989a; Fehsenfeld et al., 1990). Species shown to produce no measurable interferences at their normal atmospheric concentration ranges include NO, HNO₃, HONO, NO₃, SO₂, H₂O₂, HCHO, CO, and CO₂ (Schiff et al., 1986).

The signal below 2 ppb is nonlinear, but methods for treating the signal in the nonlinear range have been described (Drummond et al., 1989b; Kelly et al., 1990). An ozone scrubber also has been developed to minimize the ozone interference (Drummond et al., 1989a; 1989b); however, it also appears to remove up to 50% of the NO₂ at low concentrations. PAN interferences are a constant fraction of the PAN mixing ratio, although the fraction may depend on the batch and the age of the luminol solution (Sacco, 1989; Fehsenfeld et al., 1990). For a given batch of luminol, the PAN interference can be subtracted from the measured NO₂ concentration if simultaneous PAN measurements are obtained. An NO₂ reduction chamber also can be added upstream of the detector in a second sample line split off the inlet sample line (Drummond et al., 1989b; Jassim et al., 1993; Drummond et al., 1991). This allows for an ambient zero to be obtained, since the NO₂ is removed and only interferences pass through to the detector. NO₂ is then determined by difference.

A commercial luminol-based instrument is available that also measures PAN (Unisearch Associates, Inc., Ontario, Canada), which will be discussed later.

TDLAS, DOAS, and TTFMS methods were discussed earlier regarding the measurement of nitric oxide. Limits of detection for NO₂ for these methods range from about 1 ppb for DOAS to the low ppt range for TDLAS and TTFMS. During a NASA project, the TDLAS was operated aboard an aircraft by Unisearch Associates (Gregory et al., 1990b; Schiff et al., 1990). Only minor modifications were needed to the current ground-based system to make measurements aloft; however, the TDLAS showed a high bias both on the ground and in the air relative to high sensitivity chemiluminescence instruments at low concentrations. A two-photon laser-induced fluorescence system is also described by Sandholm et al. (1990) and reviewed by Parrish and Fehsenfeld (1998), however, this is strictly a research instrument. A comparison of airborne NO₂ measurements methods (O₃/NO and photolytic chemiluminescence, TDLAS, and LIF) aboard aircraft platforms was conducted by Gregory et al. (1990b). Results indicated that

at low ambient mixing ratios, below 200 ppt, the methods agreed to within 30-40 % aboard the moving aircraft platforms.

Total Reactive Nitrogen Oxides (NO_y)

As mentioned earlier, NO_y refers to the true sum of all gas-phase reactive odd-nitrogen oxide species: NO + NO₂ + HNO₂ + NO₃ + PAN + NO₃ + HONO + 2N₂O₅ + aerosol nitrate + organic nitrates + etc. (Bollinger et al., 1983; Logan, 1983; Dickerson, 1985; Fahey et al., 1985; Fehsenfeld et al., 1987; Kelly et al., 1989). Measurement of NO_y is performed taking advantage of the interference of reactive nitrogen species during thermal reduction of NO₂ to NO on a gold coated surface in the presence of CO or H₂ or on a heated molybdenum oxide surface. The NO produced is subsequently detected using an O₃/NO chemiluminescence detector as describe earlier. To avoid losses in the sampling line and inlet, the reduction chamber is moved to the front of the inlet line, which results in only NO passing through the inlet line to the detector. Thermal Environmental Inc. manufactures the only commercially available NO_y monitor. They modify their standard and high sensitivity units, moving the reduction chamber to the inlet. These units or individually modified units have been used in recent ozone and aerosol field programs (Wright and Roberts, 1996; Blumenthal et al., 1997b). Comparison of NO_y monitors using different reduction surfaces have been performed at the surface and aloft (Fehsenfeld et al., 1987). Parrish and Fehsenfeld (1998) review these comparisons and indicate that while these monitors are suitable for measurements at ground level, problems have been noted for measurements aloft from aircraft platforms.

Nitrate Radical (NO₃)

Measurement of nitrate radical is important for understanding nighttime production of HNO₃, which can be an important pathway for removal of NO₂ from the atmosphere (Smith et al., 1995). It also may be important in the formation of HNO₃ under wintertime cloudy conditions in the western US where high levels of aerosol nitrate are observed during extended cool foggy periods, e.g., San Joaquin Valley of California.

The nitrate radical is measured at the ppt concentration level and nearly free from interferences by DOAS (Plane and Nien, 1992; Winer and Biermann, 1989 and references cited therein; Biermann et al., 1988; Finlayson-Pitts and Pitts, 1986 and references cited therein; Plane and Smith, 1995). Detection limits for nitrate radical by DOAS are in the few ppt range (Smith et al., 1995). The method is briefly described earlier under the nitric oxide section. Instruments are available commercially from several sources.

Nitrous Acid (HNO₂)

Continuous and integrated methods have been developed for the measurement of HNO₂ or as it is often written, HONO. Continuous methods rely on the spectroscopic determination of HONO, while integrated methods rely on the collection of HONO on a reactive surface followed by subsequent analysis of nitrite by either colorimetric methods or ion chromatography. Spectroscopic methods include TDLAS, DOAS, and FTIR. The latter has a poor detection limit for HONO, on the order of 10 ppb (Tuazon et al., 1980), which makes the method not suitable for most ambient applications. DOAS, described above, has reported limits of detection below about 0.5 ppb (Platt and Perner, 1980; Appel et al., 1990; Winer and Biermann, 1989). Appel et al. (1990) compared a DOAS to the annular denuder method. The methods were highly correlated ($r=0.94$) and on the average agreed to within 10%, with DOAS showing a systematic high bias of 10%. Uncertainty in the DOAS measurement for HONO was estimated at about 30%. An additional spectroscopic method is described in Parrish and Fehsenfeld (1998), UV-photofragment/LIF, but it has been applied in only a limited sense and will not be described here. Time-integrated methods, for the determination of HONO, employing a collection surface or substrate followed by chemical analysis in the laboratory will be discussed later in Section A.2.

Peroxyacetyl Nitrate (PAN) and Other Organic Nitrates

Two GC methods and two spectroscopic methods are available to measure PAN in the troposphere. The two GC methods differ in their detector, one being an electron capture detector (GC-ECD) and the other being the luminol chemiluminescence detector (GC-L). PAN has most often been measured in the troposphere using GC-ECD (Singh and Salas, 1983; Drummond et al., 1989a, 1989b; Blanchard et al., 1990; Ridley et al., 1990; Williams and Grosjean, 1990 and references cited therein). However, GC-ECD instruments specifically designed to measure PAN in ambient air are not available commercially. In the GC-ECD method, PAN is separated from other reactive nitrogen oxides, including other organic nitrates by gas chromatographic and then determined based on its retention time by the ECD. Calibration of the detector requires the injection of PAN into the system. Quantification is usually based on peak area.

The GC luminol method was first described by Burkhardt et al. (1988). In this method, PAN is separated from NO₂ and other organic nitrates by gas chromatography, as with the GC-ECD. However, PAN eluting from the GC column is thermally reduced to NO₂ prior to detection, and then measured using the same luminol detector as described above for the luminol chemiluminescence measurement of NO₂. The more reactive oxides of nitrogen, such as HNO₃, HONO, NO₃, and other reactive interfering species, such as ozone, are retained on the column (Burkhardt et al. 1988). NO, while passing through the GC column, is not detected by the luminol detector. This method is available commercially.

The GC-L method has been compared to the GC-ECD methods (Drummond et al., 1990; Blanchard et al., 1990, also see Solomon and Thuillier, 1994). In general, the results indicated that the two methods agree to within 20-30 percent and that the GC-L method can provide accurate, continuous, and sensitive measurements of ambient PAN concentrations down to about 25 ppt (Blanchard et al., 1990).

One major advantage of the GC-L PAN monitor compared to the GC-ECD is the method of calibration. The GC-ECD requires calibration by PAN in the field, which is difficult to do accurately because of the poor stability of PAN at ambient temperatures;

although methods have been described (see for example Gregory et al. 1990c). On the other hand, the GC-L instrument is calibrated in the laboratory with PAN under controlled conditions to obtain the column efficiency, and then the detector can be calibrated in the field with NO₂, which is much more stable than PAN. This advantage is realized since PAN is quantitatively converted to NO₂ before detection, and the luminol detector is specific for NO₂.

The first use of the luminol PAN instruments in a regional study in the US was during the 1990 San Joaquin Valley Air Quality Study. PAN monitors (Unisearch Model LPA-4) were operated for nearly 2 months at 10 sites and collocated with a suite of other gas-phase and aerosol phase measurements (see Solomon, 1994b for a description of the study). The PAN monitors were calibrated in the laboratory with PAN prior to shipping and several times in the field, as well. For one week during the study, the luminol monitor was compared to a GC-ECD. Results indicated a significant bias between the two monitors. A detailed laboratory experiment comparing the two monitors was conducted immediately after the study, using simultaneous sampling from a chamber. Results were more consistent after correcting a problem with the calibration of the GC-ECD. An overall uncertainty was assigned to the PAN luminol measurements of about 25% (see Solomon and Thuillier, 1994).

In situ atmospheric concentrations of PAN are determined by measuring the absorption of PAN in the infrared wavelength region. When applied to ambient measurements, FTIR is combined with a long-pathlength, multiple-reflectance system to yield optical pathlengths of 1-2 km (Biermann et al., 1988 and references cited therein; Finlayson-Pitts and Pitts, 1986 [see pp. 319-337 for a brief summary of the technique and additional references]). Moderately low limits of detection (<a few ppb), applicable to ambient measurements in polluted air are obtained by the use of long-pathlengths. This is a direct measurement of PAN and ambient concentrations are determined from absorption coefficients. Therefore, this is an absolute, highly specific, nearly interference-free measurement method that can be considered as a reference method (Biermann et al., 1988; Hering et al., 1988).

Besides PAN, a number of other species can be measured by long-path FTIR, including HNO₃, NH₃, HCHO, and HCOOH. Detection limits for these species are about

1-4 ppb (Biermann et al., 1988; Finlayson-Pitts and Pitts, 1986 [see pp. 319-337]). This poor sensitivity, relative to many of the other methods, is considered to be the major disadvantage of the method. However, since the FTIR is considered a reference method, it is recommended for QA/QC purposes, especially since PAN, HNO_3 , and NH_3 concentrations can be measured simultaneously.

PAN can also be measured at ppt concentrations by TTFMS as described above.

PAN is the dominant organic nitrate species found in ambient air and is observed in urban areas at peak concentrations of a few ppb to tens of ppb (Grosjean, 1983; Tsalkani et al., 1991; Solomon and Thuillier, 1994). Measurement of other organic nitrate compounds have been obtained in several areas as well, typically with total concentrations of only a few hundred ppt (Flocke et al., 1991; O'Brian et al., 1995). These species are determined by collection on charcoal traps, Tenax, or cooled glass beads and quantified by GC-ECD, GC-L, or GC-chemiluminescence as described earlier (Atlas and Schauffler, 1991; Bertman et al., 1995; O'Brian et al., 1995; Hao et al., 1994; Flocke et al., 1991). O'Brian et al. (1995), for example, quantified 17 organic nitrates in atmospheric samples collected at a rural site in Ontario, Canada using charcoal traps and quantified using both GC-ECD and GC-L methods. The concentration of total organic nitrates ranged from 12-140 ppt, excluding PAN. Measurement of these species helps to understand peroxy radical chemistry, as the peroxy radicals are precursors to these species and play a significant role in the ozone formation processes (see discussions in Flocke et al., 1991 and in Finlayson-Pitts and Pitts, 1986).

Nitric Acid (HNO_3)

Continuous and integrated methods have been developed for the measurement of HNO_3 . However, suitable (continuous, high sensitivity, easy to use) methods are not yet available; although a new approach is undergoing evaluation and field testing (Edgerton, 1998, private communication) and will be briefly described below. The most widely used methods involve the use of reactive filters and/or diffusion denuders (see for example Lawson, 1988 for results of an extensive intercomparison of many of these methods). These methods have been problematic due in part to the partition of nitrate

among the gas, particle, and liquid droplet phases, which is a function of temperature, relative humidity, aerosol composition, and the reactive nature of HNO_3 (Hildemann et al., 1984; Russell and Cass, 1986). Filter and denuder based methods for determining time-integrated concentrations of HNO_3 are discussed in Section A.2.

Several research methods, based on spectroscopic determination of HNO_3 , with varying levels of sensitivity, have been developed; however, they require highly trained operators. Spectroscopic methods include TDLAS, FTIR, and TTFMS. These methods have been described earlier in regards to the determination of NO and PAN. Detection limits for these methods for HNO_3 range from about 4 ppb for FTIR, to about 0.5 ppb for TDLAS, to less than 0.001 ppb for the TTFMS. Of these methods, only the TDLAS is available commercially, yet it still requires a well-trained operator. TDLAS was compared to a filter-based method and a denuder method for the collection of HNO_3 aboard aircraft (Gregory et al., 1990d). Results were mixed and at times differed by a factor of two at HNO_3 concentrations < 500 ppt.

A recently developed method, chemical ionization mass spectroscopy, provides for the continuous, fast-response, molecular-specific determination of HNO_3 with limits of detection in the 10 ppt concentration range (Huey et al., 1998; Mauldin et al., 1998). However, as with the spectroscopic methods, the CIMS is still in the research stage of development. CIMS is not a direct measurement of HNO_3 , but relies on the equilibrium between HNO_3 and a reactant ion, e.g., SiF_5^- or HSO_4^- (Huey et al., 1998; Mauldin et al., 1998). Comparison of CIMS with filter packs for the measurement of HNO_3 (Fehsenfeld et al., 1998) reaffirmed that the collection of HNO_3 by Teflon/nylon filter packs results in a positive bias for HNO_3 due to volatilization of particulate ammonium nitrate from the Teflon pre-filter (see e.g., Hering et al., 1988 and references cited therein).

A recently developed method (Edgerton, 1988, private communication) uses two high sensitivity NO_y monitors and a nylon filter on one channel to remove HNO_3 from that channel. Nitric acid is then determined by difference. The method is currently being evaluated.

Ammonia (NH₃)

Continuous and integrated methods have been developed for the measurement of NH₃ in the troposphere. The most widely used methods, historically, involve the use of reactive filters and/or diffusion denuders (see for example Wiebe et al., 1990; Appel et al., 1988 for results of an extensive intercomparison of many of these methods). Filter and denuder based methods for determining time-integrated concentrations of NH₃ are discussed in Section A.2.

Recently, an O₃/NO chemiluminescence monitor has been modified to measure NH₃ continuously with a limit of detection around 1 ppb (Kita, Thermal Environmental Instruments, private communication). This continuous sampler has a proprietary converter that allows for the measurement of NO, NO_x or NO_y, and NH₃ separately by switching between three channels rather than two as is done in the standard NO/NO_x/NO_y monitor. This is a relatively new instrument, that is commercially available. The monitor needs to be calibrated in the field with NH₃, and low levels of NH₃ are difficult to obtain. NH₃ losses in the inlet and tubing to the monitor can severely limit levels of detection in ambient air (Parrish and Fehsenfeld, 1998). However, this is the only continuous commercially available method that has low limits of detection and does not require highly trained operators. Calibration and long inlet lines can be problematic however.

Several continuous wet chemical flow techniques are summarized in Parrish and Fehsenfeld (1998). Of the methods reviewed by these authors, the one that showed the most promise for continuous NH₃ measurements was described by Genfa et al. (1989). In this method, NH₃ diffuses through a porous membrane into water where the dissolved NH₃ reacts with a reagent that results in fluorescence from the reaction product. The method is calibrated against known standards, is relatively inexpensive, is specific for NH₃, and has a limit of detection below 50 ppt for a 5-min average sample time.

Several spectroscopic methods for the determination of NH₃, with varying levels of sensitivity, have been developed; however, most require highly trained operators. Spectroscopic methods include TDLAS, DOAS, FTIR, and TTFMS. These methods have been described earlier with regards to the determination of NO and PAN. Detection

limits for NH_3 by these methods range from about a few ppb or less for FTIR and DOAS, to about <0.5 ppb for TDLAS, to less than 0.001 ppb for the TTFMS. Of these methods, only DOAS is available commercially.

As mentioned for the measurement of HNO_3 , chemical ionization mass spectroscopy, appears to be promising for the determination of NH_3 with limits of detection in the low ppt concentration range (Ziereis and Arnold, 1986; also see Parrish and Fehsenfeld, 1998). However, as with the spectroscopic methods, the CIMS is still in the research stage of development and requires highly trained personnel to operate. Parrish and Fehsenfeld (1998) also mention several other research grade methods for measuring NH_3 , including CO_2 differential absorption lidar (DIAL) and an LIF method. The reader is referred to Parrish and Fehsenfeld (1998) for additional information on these methods.

The National Oceanic and Atmospheric Administration (NOAA) will be conducting an NH_3 methods comparison during the winter of 1998-1999. The study will involve comparison of a high time resolution citric acid denuder-filter pack system, a modification of the ozone/ NO chemiluminescence system described above, and a CIMS. Results from this evaluation should provide additional information on the precision, accuracy, and reliability of these methods to measure ambient ammonia concentrations in a nearly continuous manner (Fehsenfeld, NOAA, private communication, 1998).

A.1.2 Carbon-Containing Species

Compounds in the gas-phase containing carbon represent an extremely complex mixture in the atmosphere. The most abundant species are CO , CO_2 , and CH_4 , however, hundreds of species containing carbon, hydrogen, and heteroatoms, such as oxygen and nitrogen are also present in the gas-phase. This section describes methods for the measurement of CO , CO_2 , and CH_4 , of hydrocarbons containing only carbon and hydrocarbons, and of oxygenated hydrocarbon species. Major subgroups include non-methane hydrocarbons (hydrogen and carbon compounds only) and volatile organic compounds (VOC) containing hydrogen, carbon, and possibly oxygen.

Carbon Monoxide (CO)

The EPA reference method for measuring CO continuously in air uses non-dispersive infrared spectroscopy (NDIS) (Informatics, 1979). A time-integrated method is below. In NDIR spectroscopy, infrared light from a conventional light source passes through two parallel cells, one which is the reference cell and contains a non-adsorbing gas and the other the sample cell with ambient air passing continuously through it. The difference in the signals is proportional to the CO concentration in air and quantitative results can be obtained when calibrated against known standards. The limit of detection for CO is about 1 ppm, which is well below concentrations observed in ambient air. Lower limits of detection (<100 ppb) also have been obtained with a modified gas filter correlation NDIS (Dickerson and Delany, 1988). TDLAS is capable of measuring CO at levels below 250 ppt. An intercomparison of the gas filter correlation (GFC) NDIS and TDLAS showed agreement to better than 10 % (Fried et al., 1991). The precision of the GFC NDIS was about 10% and that of the TDLAS was about 4%. Several other continuous spectroscopic and chemical methods are described in Parrish and Fehsenfeld (1998) and in Finlayson-Pitts and Pitts (1986) and the reader is referred to these sources for more information. Parrish and Fehsenfeld (1998) also describe a recently developed method based on vacuum UV excited resonance fluorescence of CO that is sensitive (less than 1 ppb), precise (about 1-2 ppb), and accurate with a high time resolution, which makes it suitable for use aboard aircraft. An intercomparison between the UV instrument and TDLAS showed agreement to within 10 % on aircraft flights.

A time-integrated method for CO involves collection of an air sample in a pretreated canister followed by gas chromatographic separation followed by reduction of CO to CH₄ with detection by a flame ionization detection (GC-FID). The GC-FID method is described in more detail below, as determination of CO is obtained in conjunction with determination of non-methane hydrocarbon measurements.

Non-Methane Hydrocarbons (NMHC), CO, CO₂, and CH₄

Measurements of NMHC (usually in the C₂-C₁₀ carbon number range, although recent work has expanded the range to C₂₀+) typically requires collection of a sample in the field, followed by chemical analysis of the sample in a laboratory at a later time. NMHC species contain, by definition, only hydrogen and carbon atoms. VOC species, which will be discussed later, include NMHC plus oxygenated hydrocarbons and perhaps other heteroatoms, which have been recently identified as comprising a significant fraction of the unidentified VOC, especially in rural areas (Rassmussen, personal communication). NMHC samples are collected in the field in canisters (C₂-C₁₀) or in cartridges containing an adsorbent (C₈-C₂₀+) . Two analytical methods are generally used to determine concentrations of NMHC: GC-FID and GC-mass spectroscopy (GC-MS). GC-FID measures only NMHC under normal operating conditions and typical urban and rural atmospheric concentrations of hydrocarbons. FID is non-specific for hydrocarbons, thus the need to separate species using gas-chromatography, and has a sensitivity that is approximately linearly proportional to the number of carbon atoms in the hydrocarbon molecule (Ackman, 1968). GC-MS, on the other hand is capable of measuring NMHC and oxygenated hydrocarbons. In addition to NMHC, GC-FID also provides concentrations of CO, CO₂, and CH₄. A listing of typical NMHC species found in urban environments is given in Table A-2. Several low molecular weight oxygenated compounds are also listed. However, this list represents only the species typically determined for input to photochemical emissions-based models. Hundreds of compounds have been identified in tunnel studies and in the ambient environment when consideration is given to identifying peaks in the chromatogram that are typically referred to as “unidentified” (Gertler et al., 1996).

Speciated hydrocarbons also can be measured semi-continuously (one or two samples per hour) in the field using automated GC-FID, as is used in the Photochemical Assessment Monitoring Stations (PAMS) (Oliver et al., 1996). The number of species obtained using the automated method is more limited than those using time-integrated sampling followed by chemical analysis in the laboratory. Greenberg et al. (1994), Greenberg et al. (1996), Bottenheim et al. (1997), and Goldan et al. (1995) describe an

Table A-2. VOC Species and Corresponding Abbreviations.

Species	Abbreviation	Carbon Number	Functional Group
ethane	ethane	2	alkane
ethene	ethene	2	alkene
ethyne	ethyne	2	alkene
propane	propane	3	alkane
propene	propene	3	alkene
isobutane	ibutane	4	alkane
isobutene	Ibutene	4	alkene
1-butene	x1buten	4	alkene
1,3-butadiene	x13butad	4	alkene
butane	Butane	4	alkane
trans-2-butene	t2buten	4	alkene
2,2-dimethylpropane	x22dpro	4	alkane
cis-2-butene	c2buten	4	alkene
3-methyl-1-butene	x3mbute1	5	alkene
isopentane	Ipentane	5	alkane
1-pentene	Pentene1	5	alkene
2-methyl-1-butene	x2m1bute	5	alkene
pentane	Pentane	5	alkane
isoprene	Isoprene	5	alkene
trans-2-pentene	t2penten	5	alkene
cis-2-pentene	c2penten	5	alkene
2-methyl-2-butene	x2m2bute	5	alkene
2,2-dimethylbutane	x22mbuta	6	alkane
cyclopentane	Cypentan	5	alkane
2,3-dimethylbutane	x23mbuta	6	alkane
cis-4-methyl-2-pentene	c4mpnte2	6	alkene
2-methylpentane	x2mpenta	6	alkane
3-methylpentane	x3mpenta	6	alkane
2-methyl-1-pentene	x2mpnte1	6	alkene
1-hexene	x1hexene	6	alkene
hexane	Hexane	6	alkane
trans-2-hexene	t2hexene	6	alkene
2-methyl-2-pentene	x2m2pnte	6	alkene
cis-2-hexene	c2hexene	6	alkene
methylcyclopentane	Mcypenta	6	alkane
2,4-dimethylpentane	x24mpnta	7	alkane
benzene	Benzene	6	aromatic
cyclohexane	Cyhexane	6	alkane
2-methylhexane	x2mhexas	7	alkane

Table A-2. VOC Species and Corresponding Abbreviations (continued)

Species	Abbreviation	Carbon Number	Functional Group
2,3-dimethylpentane	x23mpnta	7	alkane
3-methylhexane	x3mhexan	7	alkane
heptane	Heptane	7	alkane
methylcyclohexane	Mcyhexan	7	alkane
4-methyl-1-pentene	x4mpnte1	6	alkene
2,4,4-trimethyl-2-pentene	x244t2pe	8	alkene
2,5-dimethylhexane	x25mhexa	8	alkane
2,4-dimethylhexane	x24mhexa	8	alkane
2,3,4-trimethylpentane	x234mpta	8	alkane
toluene	Toluene	7	aromatic
2,3-dimethylhexane	x23mhexa	8	alkane
2-methylheptane	x2mhepta	8	alkane
3-ethylhexane	x3ethexa	8	alkane
2,2-dimethylheptane	x22mhept	9	alkane
2,2,4-trimethylhexane	x224mhxa	9	alkane
octane	Octane	8	alkane
ethylcyclohexane	Etyhexa	8	alkane
ethylbenzene	Etbenzen	8	aromatic
m&p-xylene	Mpxylene	8	aromatic
styrene	Styrene	9	aromatic
o-xylene	Oxylene	8	aromatic
nonane	Nonane	9	alkane
isopropylbenzene	Iprobenz	8	aromatic
n-propylbenzene	Nprobenz	8	aromatic
p-ethyltoluene	Petoluen	9	aromatic
o-ethyltoluene	Oetoluen	9	aromatic
m-ethyltoluen	Metoluen	9	aromatic
1,3,5-trimethylbenzene	x135tmbz	9	aromatic
1,2,4-trimethylbenzene	x124tmbz	9	aromatic
decane	Decane	10	alkane
a-pinene	Apinene	10	alkene
b-pinene	Bpinene	10	alkene
methylstyrene	Mstyrene	10	aromatic
1,2,3-trimethylbenzene	x123tmbz	9	aromatic
1,3-dimethylbenzene	x13dbenz	8	aromatic
1,4-dimethylbenzene	x14dbenz	8	aromatic
2,4,4-trimethyl-1-pentene	x244t1pe	8	alkene
formaldehyde	formalde	1	carbonyl
acetaldehyde	acetalde	2	carbonyl

Table A-2. VOC Species and Corresponding Abbreviations (continued)

Species	Abbreviation	Carbon Number	Functional Group
Acetone	acetone	2	carbonyl
propanal	propanal	3	carbonyl
methylethylketone & butanal	mekbut	4	carbonyl
pentanal & pentanone	penpan	5	carbonyl
cyclohexanone	cyhex	6	carbonyl
hexanal & hexanone	hexhex	6	carbonyl
benzaldehyde	benzalde	7	carbonyl

automated system with comparisons to the canister method. Several other methods for the determination of organic species in ambient air are in development. These have been summarized by Parrish and Fehsenfeld (1998).

Hydrocarbon Sample Collection

Intermittent, time-averaged ambient air samples for hydrocarbon species analysis are usually collected in SUMMA[®] polished stainless steel canisters of various sizes (e.g., 6 l for surface and 0.85 l for aircraft measurements) (see description of method in Solomon and Thuillier, 1994 as specified by Rasmussen). These canisters are also analyzed for CO, CO₂, and CH₄. Stability of the hydrocarbons in these canisters during storage is good for most compounds; although losses of higher molecular weight species have been noted as well as a positive artifact for olefins (Holdren, 1979; Rasmussen, 1997 personal communication; Solomon and Thuillier, 1994 for results during SJVAQS). Finally, results of storage depend on the history of use and handling of the canister. Canisters need to be thoroughly cleaned before use and this process has been described by Rasmussen (1989) as adopted from EPA Method TO-14 (Winberry et al., 1988). A summary of the procedure is given in Solomon and Thuillier (1994) as applied in during the 1990 SJVAQS. Tedlar bags are also used for surface measurements following the same approach as for cannisters.

For collection of higher molecular weight hydrocarbons (C₁₀-C₂₀), samples are collected using cartridges filled with Tenax. Ambient air is drawn through these cartridges at constant flow rate, and then the samples are brought to the laboratory for chemical analysis (Biesenthal et al., 1997; also see description of method in Solomon and Thuillier, 1994 as specified by Rasmussen). Samples collected using TENAX can be analyzed by GC-MS, which also provides an estimate of higher molecular weight oxygenated compounds if large sample volumes are used. Measurement of low molecular weight carbonyl compounds, using a different adsorbent and analyzed by GC-liquid chromatography will be discussed later.

CO-CH₄-CO₂

After sample collection in canisters, CO-CH₄-CO₂ are determined by EPA method TO-12. In this method, these species are separated by gas chromatography using a packed column. Methane (CH₄) is measured directly by a flame ionization detector (FID), while CO and CO₂ are first reduced to CH₄ over a Ni catalyst at 400°C and reported as CH₄. An example of operating conditions is given in Solomon and Thuillier (1994).

Total Non-Methane Hydrocarbon (TNMHC)

Total non-methane hydrocarbon in canisters is routinely determined using GC-FID according to the guidelines specified in EPA Method TO-12, as described above for CO-CO₂-CH₄. An example of operating conditions is given in Solomon and Thuillier (1994). This method detects hydrocarbons (compounds containing only hydrogen and carbon) with great sensitivity as well as hydrocarbons containing elements other than carbon and hydrogen (i.e., oxygen, chloride, and other heteroatoms). However, hydrocarbons containing heteroatoms are typically below the detection limit of the GC-FID, under usual operating conditions and sample size. However, because heteroatoms can be detected by this method, TNMHC is sometimes referred to as total non-methane organic carbon (TMNOC). Use of TNMHC implies that species containing other elements are corrected for or ignored.

C₂ - C₁₀ Hydrocarbon Speciation Method

The method most often used for analysis of hydrocarbon species is EPA Method TO-14. This method is for analysis of hydrocarbons collected in SUMMA[®] canisters with analysis by GC-FID. An example of operating conditions is given in Solomon and Thuillier (1994) and Bottenheim et al. (1997). The GC-FID method typically uses a 500 ml sample. The method has been modified slightly by removing the dryer to prevent loss of monoterpenes. Samples are analyzed by directly trapping a 250 or 500 ml aliquot of

the sample on a stainless steel loop cold trap containing glass beads immersed in liquid oxygen. The trapped hydrocarbons are then desorbed into a capillary cryofocusing loop and separated using gas chromatography. Details of the procedure as applied by Rasmussen for samples collected during SJVAQS is given in Solomon and Thuillier (1994) and during Pacific '93 by Bottenheim et al. (1997). Detection limits observed during SJVAQS, by individual species, are given in Solomon and Thuillier (1994), and are in the range of 0.1-0.2 : g m⁻³ or about 0.2 ppbC. Precision, based on analysis of duplicate samples collected during SJVAQS, is given for a series of compounds in Solomon and Thuillier (1994). Precision values for the most abundant species were in the range of 10-20 %. Poorer precision (in the range of 40-80 %), was reported for aromatic compounds and was likely do to the low ambient concentrations of these species in the duplicate samples. A discussion of a methods intercomparison study and of several methods still in development for determination of hydrocarbon species is described in Parrish and Fehsenfeld (1998).

C₇-C₂₀ Hydrocarbon (VOC) Speciation Analysis

For over 20 years, the analysis of VOC compounds in ambient urban air for C₂ to C₁₀ hydrocarbon speciation has been performed on air sample volumes of 100 to 500 ml. Standardization of GC-FID methods around these small volumes has been done (1) because this provides sufficient concentrations to accurately measure the C₂ to C₁₀ hydrocarbons in urban air in one processing step; (2) processing larger volumes of air is difficult, usually requiring several preparatory steps before the sample is cryofocused on the head of the column, and (3) due to the problem of frequent freeze-up [blockage] of the freezeout loop by the water vapor in sample volumes larger than 500 ml. Nafion[®] and other selective dryers have been used to remove the water, but all of them have some inherent problem. For example, Nafion[®] destroys most of the C₁₀H₁₆ monoterpenes. Rasmussen (personal communication) has developed a single pre-concentration step to allow larger volumes (1,000 - 5,000 ml) of air to be used with a freezeout loop. Details of this method are given in Solomon and Thuillier (1994).

A comparison of the conventional method, using a 500 ml sample, to the improved method using the larger sample volume, both followed by GC-FID analyses was performed on 155 SJVAQS samples. The majority (>90%) of samples had TNMHC concentrations less than 200 ppbC. Correlation coefficients (r^2) for most species compared were greater than 0.9 with an average r^2 value of 0.946 for total identified non-methane hydrocarbons. The r^2 agreement between the methods for the total non-methane hydrocarbon values (identified plus unidentified) was 0.823. This is because the total unidentified hydrocarbon fraction compared with and a r^2 value of only 0.254. Obviously, the two methods do not agree on the amount of the unidentified hydrocarbons in their respective chromatograms; the method using a higher sample volume reports a smaller quantity of unidentified species in the C_5 to C_{10} range. Since the method was developed with the objective of analyzing a 10-fold larger sample, to better measure the C_{10+} species, many of the small baseline peaks not normally seen or integrated by the conventional method in a 100-500 ml sample are now being better determined and identified. The only serious problem with the improved method is that two of the C_2 species (ethylene and acetylene) are poorly separated by the Carbotrap III sorbent bed when used with the 5000 ml samples. The r^2 , between the two methods, for these compounds is poor, 0.23 and 0.06, respectively. Surprisingly, ethane is well separated with a r^2 value of 0.90. However, what was lost in the chromatography of the C_2 fraction in the 5000 ml sample is gained in the higher molecular weight hydrocarbons, those species containing more carbons than decane (C_{10}).

“What percentage of the total VOC or hydrocarbon burden is in the C_{10} to C_{15} fraction?” is an important question. At present the California Air Resources Board (ARB) assumes that 3% of the TNMOC are greater than C_{10} . From the analysis of the 155 SJVAQS/AUSPEX samples, using the improved method, a more robust value of $8 \pm 4\%$ was measured. In this analysis, attention was focused on rural to cleaner suburban air samples with TNMOC values of 25 to 100 $\mu\text{g}/\text{m}^3$. No attempt was made to measure urban samples with concentrations of 200-500 $\mu\text{g}/\text{m}^3$, which possibly are more typical of the types of samples previously analyzed by ARB.

To verify GC-FID peak identifications and to determine what other NMHC compounds might be present in ambient air, samples also are analyzed by GC-MS full scan. This approach requires sample volumes from 500 ml (verification of GC-FID peaks) to sample volumes typically, in the range of 5000 to 50,000 ml. The larger sample size allows for determination of many of the smaller peaks that were in the conventional method, but too small for identification and quantification. GC-MS full scan sensitivities for most compounds are at 0.1 ppb or less (see Solomon and Thuillier, 1994 for SJVAQS). Bottenheim et al. (1997) report limits of detection in the range of 5-30 ppt with precision in the range of 20-40 ppt. Results from an intercomparison conducted by the National Center for Atmospheric Research, indicated agreement between participating laboratories of 3-15 %.

Oxygenated Volatile Organic Compounds

Historically, more than 80-90 % of the hydrocarbon mass are identified by species in hydrocarbon samples collected in urban areas, whereas only 40 to 50% of the mass is identified in samples collected downwind of urban and rural areas (e.g., Magliano, 1996; Rasmussen, 1996; Lonneman and Seila, 1989). Recent results indicated that many of the unidentified peaks are oxygenated hydrocarbons (Rasmussen, 1996; Rasmussen, personal communication regarding results in SJVAQS, NARSTO-NE).

Over the last 10 years, low molecular weight ($<C_7$) carbonyl species (aldehydes and ketones) have been the primary oxygenated species measured during regional field campaigns (see those listed at the end of Table A-2). More recently, a number of other species, as well as the low molecular weight carbonyls have been measured, including alcohols, esters, heterocyclic compounds, and carbonyl compounds (see Table A-3).

The standard method for measuring low molecular weight carbonyl compounds involves the collection of these species using C_{18} Sep-Pak cartridges that have been impregnated with purified 2,4-dinitrophenylhydrazine (DNPH) and phosphoric acid (Fung and Grosjean, 1981; Tejada, 1986; Grosjean and Grosjean, 1995 and references

Table A-3. Oxygenated Hydrocarbon Analysis: GC-MS Sample Specifications

Alcohols	Aldehydes	Ketones
Ethanol	Acetaldehyde	Acetone
2-Propanol	Acrolein	Methyl-Vinyl Ketone
2-Methyl-2propanol	Propanal	2-Butanone
1-Propanol	2-Methylpropanal	3-Methyl-2-butanone
2-Butanol	Methacrolein	2-Pentanone
3-Methyl-1-pentanol	Butanal	4-Methyl-2-pentanone
1-Hexanol	2-Butenal	2-Hexanone
2-Ethyl-1-hexanol	Pentanal	4-Heptanone
	Hexanal	2-Heptanone
Esters	Heptanal	Cyclohexanone
Methyl Formate	Benzaldehyde	3-Heptanone
Ethyl Acetate	Octanal	6-Methyl-2-heptanone
Butyl Formate	Nonanal	6-Methyl-5-heptan-3-one
Butyl Acetate	Decanal	2-Octanone
Heptyl Formate	Cinnamaldehyde	Acetophenone
	Undecanal	2-Nonanone
Heterocyclic Compounds		2-Decanone
Furan		2-Undecanone
2-Methylfuran		
3-Methylfuran		
Tetrahydrofuran		

cited therein; Shepson et al., 1991; Grosjean and Grosjean, 1996). Detection limits less than 0.5 ppb have been obtained. Impingers have also been used; however, limits of detection are around 1-2 ppb (Kuwata et al., 1979; Grosjean and Fung, 1982). When ambient air is drawn through the cartridge containing DNPH, carbonyl species in the air sample react with DNPH to form hydrazones, which are separated and quantified using high-pressure liquid chromatography (HPLC) in the laboratory. Carbonyl species also have been quantified using GC-FID with detection limits ranging from <10 to 200 ppt (compound dependent) (Montzka et al., 1993).

Low molecular weight (<C₁₀) volatile organic hydrocarbons can also be collected using canisters with analysis by GC-FID employing larger sample volumes or with GC-MS as described above for non-methane hydrocarbon species determination (Rasmussen, personal communication; and described in Solomon and Thuillier, 1994). The larger sample volumes, with either GC-FID or GC-MS, allow for identification and quantification of species that are normally below the limit of detection of the standard GC-FID method. Limits of detection are around 0.1 ppbC (see Solomon and Thuillier, 1994 results from SJVAQS/AUSPEX). Higher molecular weight VOC species are collected using TENAX cartridges and analyzed using GC-MS, as described above. Table A-3 provides a partial list of oxygenated species that might be measured using TENAX collection followed by GC-MS analysis or GC-FID with extended sample volumes. Chemical ionization mass spectroscopy also has been used to detect several oxygenated hydrocarbons at very low levels (see Parrish and Fehsenfeld, 1998 for summary of method).

Formaldehyde can be measured independently by several additional techniques, including two spectroscopic methods and two wet chemical methods. The wet chemical methods have been designed into continuous flow systems for in situ measurements. These include enzymatic fluorometry in which the fluorescence from an enzyme catalyzed reaction is detected (Heikes et al., 1996; Lazrus et al., 1988) and diffusion scrubbing (Fan and Dasgupta, 1994) or a glass coil scrubber (Kelly and Fortune., 1994) in which the fluorescence from the Hantzsch reaction with formaldehyde is detected. The spectroscopic methods include TDLAS (Fried et al., 1997) and DOAS (Harder et al., 1997a), which have been briefly described above. The DNPH/HPLC method for

formaldehyde was intercompared and validated against a long-path FTIR, a DOAS, and a tunable diode laser spectrometer in the 1986 Carbonaceous Species Methods Comparison Study (CSMCS) conducted by ARB in Glendora, CA (Fung and Wright, 1990; Lawson, et al., 1990). Results from this intercomparison indicated that DNPH/HPLC could provide reliable measurements of formaldehyde. Based on this evaluation, this technique was used to measure carbonyl compounds during SCAQS (Fung, 1989) and SJVAQS/AUSPEX (Fung et al., 1994). Kleindienst et al. (1988) compared four techniques for the measurement of formaldehyde in a rural environment (CH_2O between 1-10 ppb). No systematic error was observed relative to sample spikes with and without a number of potentially interfering compounds (e.g., NO_2 , SO_2 , O_3 , and H_2O_2). Heikes et al. (1996) compared 5 methods for formaldehyde under pristine conditions (CH_2O <350 ppt). Detection limits for the methods studied ranged from <10 ppt to about 100 ppt. The methods agreed reasonably well above 200 ppt, however, random variations in blanks lead to a poor correlation between methods below 200 ppt. Other comparison studies are described in Parrish and Fehsenfeld (1998).

A.1.3 Sulfur Containing Species

Sulfur Dioxide (SO_2)

Several methods exist to measure SO_2 at ambient levels in the lower troposphere. Finlayson-Pitts and Pitts (1986) provide a listing of methods available in the mid-1980s, with relevant references. The methods listed include the paraosaniline method, which is the EPA reference method (EPA, 1982), fluorescence, GC-flame photometry, TDLAS, DOAS and several others. TDLAS and DOAS methods have been described briefly in Section A.1.1. Limits of detection for SO_2 range from 85 ppt for DOAS to 10 ppb for the reference method. Parrish and Fehsenfeld (1998) describe more recent developments in the measurement of SO_2 in the clean troposphere. Instruments described by Parrish and Fehsenfeld (1998) have limits of detection as low as a few ppt and readers are referred to references cited therein Parrish and Fehsenfeld for additional information.

Currently, the most widely used method is the pulsed fluorescence method, which is an EPA equivalent method (EPA, 1982). Fluorescence analyzers are based on the principle that SO₂ molecules absorb ultraviolet (UV) light and become excited at one wavelength, and then decay to a lower energy state emitting UV light at a different wavelength. Certain hydrocarbon compounds interfere with the method but in commercial instruments they are removed prior to the fluorescence chamber. H₂O and NO also can interfere with the measurement. The interferences are less than 1 ppb for NO and less than 3% of SO₂ reading for H₂O. The pulsating UV light source compensates for fluctuations in the UV light source. The fluorescence emitted by the excited SO₂ molecules is proportional to the SO₂ concentration and upon calibration is proportional to atmospheric SO₂ concentrations. Limits of detection are in the range of 0.06-0.2 ppb depending on the integration time. Precision is reported for commercial instruments at 1% of reading or 0.2 ppb. This is also the preferred method for use aboard aircraft platforms for the collection of SO₂. It has three advantages over the FPM described below: it uses no consumable gases, has small zero drift with altitude, and its output is easily converted to mixing ratios (see discussion in Daum and Sprinston, 1993).

SO₂ also has been measured routinely by the flame photometric method (FPM); although it is used less often now. In this method, sulfur compounds are reduced in a hydrogen-rich flame to the S₂ dimer. The emission resulting from the transition of the thermally excited dimer to its ground state at 394 nm is measured using a narrow band-pass filter and a photomultiplier tube. The response of the instrument is approximately proportional to the square of the sulfur concentration. Limits of detection with commercial instruments are in the 1 ppb range. The FPM has also been used to measure particulate-phase sulfur species, since the flame photometric detector responds to both particulate and gas-phase sulfur species. In this case, particulate sulfur compounds are measured continuously after gaseous sulfur compounds are selectively removed using a lead (II) oxide-glycerol coated denuder (Garber et al., 1983). Speciation between particulate sulfate, disulfate, and sulfuric acid by selective thermal decomposition is possible (Huntzicker et al., 1978; Cobourn et al., 1978). The FPM method has also been used aboard aircraft after appropriate modifications (see review by Daum and Springston, 1993).

Other Sulfur-Containing Compounds

Several reduced sulfur-containing compounds have been measured in ambient air. These include hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), dimethyl sulfide (DMS), CH_3SH , $\text{C}_2\text{H}_5\text{SH}$, $(\text{CH}_3)_2\text{S}$, and $(\text{CH}_3)_2\text{S}_2$. Methods for the measurement of these species require collection/preconcentration and separation of the individual compounds followed by detection by a variety of methods. Several measurement methods for obtaining atmospheric concentrations of the reduced sulfur species are described in Parrish and Fehsenfeld (1998). Collection methods include cryogenic sampling or collection on a reactive substrate (e.g., gold wool or polymers), while separation of the species is done typically using gas chromatography. Detectors include flame photometry, mass spectroscopy, and electron capture detection. Several intercomparisons of methods available to measure these species have occurred for both ground-based and airborne platforms and these, along with a brief description of the methods, can be found in Parrish and Fehsenfeld (1998). The limits of detection of research grade methods are typically below 100 ppt and even below 10 ppt. A discussion of the measurement of important sulfur containing compounds associated with fog or cloud droplets is discussed in Section A.3.

A.1.4 Atmospheric Oxidants

Ozone

Methods available to measure ozone in the atmosphere include continuous monitors that measure ozone at a single point in space over time and long-path spectroscopic methods that provide time-averaged integrated ozone concentrations over path-lengths of 10-20 km. Point measurements include ultraviolet (UV) absorption, chemiluminescence, and chemical titration. Spectroscopic methods include DOAS and LIDAR (light detection and ranging). The UV photometric method is currently the most widely used method for measuring ambient concentrations of ozone and has been

designated as an equivalent EPA method for ozone in air (EPA, 1986). The UV method is based on the absorption of ultraviolet radiation at 254 nm by ozone molecules present in the monitor's absorption cell. The ozone signal is determined by the difference between ambient air containing ozone and ambient air with the ozone removed or scrubbed. The ozone concentration in the absorption cell is directly related to the magnitude of the attenuation and with proper calibration it is directly related to ambient concentrations of ozone.

The minimum detectable level of UV monitors is about 2-5 ppb. Accuracies and precision are on the order of 10-15 percent or 2-5 ppb, whichever is larger. Interferences with the UV measurement method include any gaseous component or fine particle that absorbs or scatters light at 254 nm. Gaseous inorganic compounds normally found in the atmosphere, including NO₂ and SO₂, do not interfere, and particles are largely removed by a pre-filter. The most likely interferences with the measurement are gaseous hydrocarbon compounds that are strong absorbers at 254 nm and are either partially or completely absorbed onto the scrubber. Examples of potential interfering organic compounds are aromatic compounds, such as benzene and benzene derivatives (e.g., styrene, cresol, and nitro-aromatic species), and include species that are emitted from both anthropogenic and natural sources (Leston and Ollison, 1992; Kleindienst et al., 1993). Interferences from hydrocarbons can account for a positive interference in the UV measurement for ozone of up to 40 ppb based on the concentration of the interferences occurring during peak ozone periods (Leston and Ollison, 1992). Kleindienst et al. (1993) observed about a 3% interference with O₃ measurements at typical ambient smoggy conditions.

Water vapor may also interfere with the UV method, but the interference only occurs when water vapor concentrations are high and variable. This interference appears to be due to the condensation of water vapor on imperfect absorption cell windows, thus changing the optical properties of the absorption cell (Meyer et al., 1991). Use of absorption cell windows with fewer imperfections results in a smaller interference from water vapor.

The ozone/ethylene chemiluminescence method (ECL) is the Federal Reference Method for measuring ozone in ambient air (EPA, 1978). The ECL method is based on

the reaction of ozone with ethylene ($\text{CH}_2=\text{CH}_2$ or C_2H_4), which produces formaldehyde in an electrically excited state that transitions to the ground state emitting light in the visible range. This reaction is rapid and specific for ozone and takes place in a chamber that is coupled to a blue-sensitive photomultiplier tube. Under controlled conditions, the signal produced by the ozone-ethylene reaction is proportional to the ozone concentration in the reaction chamber and with proper calibration it is proportional to ambient ozone concentrations.

The minimum detectable level of commercial ECL monitors is about 2-5 ppb. Accuracy and precision are on the order of 10-15 percent or 2-5 ppb, whichever is larger. The only major interference for measuring ozone by the ECL method is water vapor (Lodge, 1989; Leston and Ollison, 1992; Kleindienst et. al., 1993). Other components normally found in ambient air do not interfere with the measurement of ozone by the ECL method (Hodgeson et, al., 1970; Carroll et. al., 1972). The water vapor interference results in one-hour ozone concentrations that may be high relative to a "true value", i.e., a positive interference of 3-12 percent high humidities (EPA, 1986). Because this is a direct measurement of ozone, long-term changes in water vapor will affect the measured ozone concentration. However, this interference can be adjusted for by calibrating the ECL monitors at humidities expected during peak ozone periods as suggested by EPA (1986); however, this is rarely done.

Vertical profiles of ozone are obtained along a single vertical trajectory using balloon borne ozonesondes equipped with an electrochemical concentration cell (ECC) (Komhyr, 1969). These instruments are often launched together with meteorological rawinsondes that also simultaneously measure wind speed and direction, temperature, and relative humidity (See Section A.4). The ECC is composed of platinum electrodes in neutral buffered potassium iodide solutions of different concentrations in the anode and cathode chambers. When air containing ozone is brought into the cathode portion of the cell, an electrical current is generated that is proportional to the ozone flux through the cell. Ozonesondes were used recently in the NARSTO-Northeast ozone study (Lehrman et al., 1997). Limits of detection for the units used during that study were about 2-3 ppb with a precision of about 10% (Lehrman et al., 1997). Several oxidizing species can interfere with the measurement (Barnes et al., 1985; Lehrman et al., 1997). These

include NO and PAN, which result in a positive interference, and SO₂, which results in a negative interference.

Ozone is measured remotely using DOAS, as described earlier for NO in Section A.1.1. Limits of detection are in the low ppb range with a precision of less than 30% (Plane and Nien, 1992). The limit of detection in DOAS depends on the concentration of the species present in air and its absorption coefficient, since quantification is determined by mathematically de-convoluting each species in the spectrum based on unique peaks for each species. The strongest singles are de-convoluted first as weaker singles are lost in the noise during the de-convoluting process. Ozone concentrations obtained by DOAS were compared to those obtained with UV absorption (Harder et al., 1997b) during periods of uniform ozone mixing. Results indicated agreement to within 7%, even though UV absorption is a point measurement and DOAS is a path-integrated measurement.

Vertical and horizontal cross sections or profiles of ozone are obtained remotely using differential absorption lidar (DIAL). These measurements can be obtained either at the surface, looking upward, or from aircraft using a downward facing DIAL. In this method, gas concentration profiles are determined by analyzing the lidar backscatter singles for two wavelengths, one tuned to the wavelength for the species of interest, in this case for ozone at about 300 nm and one slight off that wavelength. The difference in the magnitude between the backscatter signals at the two wavelengths is proportional to the ozone concentration. Like radar, the time for the single to return to the detector provides a measure of the distance the molecule is from the source, thus allowing for a cross section to be measured. DIAL provide nearly continuous measurements of ozone from about 50 m to 3 km with a minimal detection limit of about 10 ppb or so and depends on the wavelength employed. Ozone concentrations measured with DIAL, DOAS, and UV absorption were compared as part of the EUROTRAC Tropospheric Ozone Lidar Intercomparison Experiment (TESLAS). The methods agreed among each other within 30%.

Peroxy Radicals (HO_x , RO_x)

Peroxy radicals (HO_x) and organic peroxy radicals (RO_x) can be measured by several techniques. The chemical amplifier (CA) will be discussed here, as it is the most widely used method, while the reader is referred to Parrish and Fehsenfeld (1998) for information on the LIF-FAGE and matrix isolation electron spin resonance (MIESR) methods. LIF-FAGE measures only HO_2 , while MIESR measures HO_2 plus RO_2 . The CA technique is describe by Hastie et al. (1991), Arias and Hastie (1996), and Cantrell et al. (1993). In this method, peroxy radicals (HO_2 and RO_x) are mixed in a chemical reactor with elevated concentrations of CO and NO. The peroxy radicals enter into a chain reaction with NO and CO, oxidizing these species to CO_2 and NO_2 while recycling the HO_2 or RO_2 , thus producing a large number of NO_2 molecules per radical entering the system. The reactions and details of the system are given in Hastie et al. (1991) and Arias and Hastie (1996). Limits of detection are a few ppt and precision is given at about 35% or equal to the uncertainty of determining the chain length of the reaction. The NO_2 produced is then detected using luminol chemiluminescence as discussed earlier (See Section A.1.1). Parrish and Fehsenfeld (1998) describe results of an informal comparison of peroxy radical measurement methods between the CA and MIESR methods. The two techniques generally agreed to within 40%, except under polluted conditions, in which case the CA technique was lower than MIESR.

Hydrogen Peroxide and Organic Peroxides

Several sensitive methods have been developed and inter-compared for the measurement of H_2O_2 and organic peroxides (Staffelbach et al., 1996; Mackay et al., 1996). These include several wet chemical methods and one spectroscopic method. Wet chemical techniques include enzymatic with fluorometric detection (EDF) (Lazrus et al., 1986; Heikes, 1992), Fenton derivatization with fluorometric detection (Lee et al., 1993), and high performance liquid chromatography (HPLC) (Lee et al., 1995; Kok et al., 1995). Recent fog experiments in the California's Central Valley (see e.g., Solomon and Magliano, 1996) employed the EDF method and this will be discussed here. Readers are

referred to Parrish and Fehsenfeld (1998), Kok et al. (1995), and Lee et al. (1995) for a summary of the other two wet chemical methods.

The EDF method measures hydrogen peroxide and total organic hydroperoxides continuously using a dual channel instrument (Lazrus et al., 1986). In this method, peroxides and other soluble gases are collected in distilled water flowing through a coiled glass tube. The peroxides are then reacted with p-hydroxyphenylacetic acid and the enzyme peroxidase to produce a fluorescent biphenyl derivative. Spectroscopic monitoring of the fluorescence emission at 420 nm allows for the quantitative determination of peroxides in the aqueous solution. An estimate of the relative contribution of hydrogen peroxide to total hydroperoxides is measured by introduction of a second enzyme catalase into a second aqueous flow channel, to preferentially destroy hydrogen peroxide prior to quantification. The dual-channel instrument yields only semi-quantitative organic hydroperoxide information because catalase can also react with organic hydroperoxides. The principal interference is only problematic when the contribution of the organic hydroperoxides to total hydroperoxides exceeds 50%. In this situation, the accuracy of the hydrogen peroxide measurement is degraded significantly. However, the interference can be minimized by controlling the concentration of catalase to limit hydrogen peroxide destruction to 90% or less. However, the ability to quantify total hydroperoxides is unaffected. Calibration is accomplished with gas and liquid phase standards. The gas-phase standards permit quantification of any losses in the sample inlet lines. The method has a typical hydrogen peroxide detection limit of 20-30 ppt, with a 10% precision and 15% accuracy for gas-phase concentrations around 1 ppb. The instrument has a time response of 30 seconds.

TDLAS is the only spectroscopic method for the measurement of hydrogen peroxide (Mackay et al., 1990; Mackay et al., 1996). The method was described earlier (Section A.1.1). Limits of detection are in the range of 50-100 ppt (30 min average) with a precision of 5% over a 24-hr period with an accuracy of about 20% (Mackay et al., 1996). An intercomparison of TDLAS, EDF, and HPLC methods is described in Mackay et al. (1996) and Staffelbach et al. (1996). Results were mixed with agreement at times being as close as 20% and at other times differences being as large as a factor of 2. A summary of these intercomparisons is given in Parrish and Fehsenfeld (1998).

Hydroxyl Radical (OH)

The reader is referred to the summary of methods and intercomparisons among methods given in Parrish and Fehsenfeld (1998) and in Finlayson-Pitts and Pitts (1986). All methods described are non-routine and require skilled operators. However, the OH radical is likely the most important species to be measured to understand gas-phase oxidation processes in the atmosphere, thus it is essential to a comprehensive model evaluation (See Section 3.1). Historically, OH measurements have not been included in regional field programs due to the difficulty in the measurement, insufficient sensitivity, and problems with interferences. Current methods can now provide sufficient sensitivity (Parrish and Fehsenfeld, 1998). Methods described include fluorescence assay by gas expansion-LIF (FAGE-LIF), long-path absorption, and chemical ionization mass spectroscopy (CIMS).

A.1.5 Hydrochloric Acid (HCl)

Hydrochloric acid can be monitored continuously by TDLAS (Pokrowsky and Herrmann 1981) with limits of detection below 1 ppb. More often, time-integrated measurements are obtained using denuders (Solomon et al., 1988a; Eldering et al., 1991). The TDLAS method was described earlier (see Section A.1.1) and the denuder methods are described in Section A.2.

A.2 Measurements of Particulate Matter and Condensable Gases

This section presents methods commonly used to measure fine particle mass and its chemical components. Our intent is not to provide an exhaustive list of methods and their descriptions, since these methods are presented in different EPA reports and many have been recently reviewed by Chow (1995). Rather, we provide an overview of existing methods that can be used to select the most appropriate methods when designing a field program. Table A-4 provides a summary of the major methods available for the

Table A-4. Measurements of Particulate Matter (Mass and Chemical Composition by Filter-Based and Continuous In-Situ Methods).

Method	Parameter	Detection Limit	Precision	Accuracy	Interferences	References
Teflon Filter/Gravimetric (FRM)	Mass	2 $\mu\text{g}/\text{m}^3$	5%	Since this is the FRM its accuracy is by definition 0%, however it is not possible to quantify it because there is no gold standard for particle mass	It does not collect all semivolatiles such as ammonium nitrate and organic carbon	Federal Register (1997)
Teflon Filter/IC	Sulfate	0.64 $\mu\text{g}/\text{m}^3$	5%	5-10	none	Koutrakis et al. (1988); Solomon et al. (1988)
Teflon Filter/IC	Ammonium	0.1 $\mu\text{g}/\text{m}^3$	5%	5-10	none	Koutrakis et al. (1988); Solomon et al. (1998)
Teflon Filter/pH	Hydrogen Ion	2.4 nmole/ m^3	5-10%	10-20%	Alkaline particles, some weak acids	Koutrakis et al. (1992)
Nylon Filter/IC	Nitrate	0.04 $\mu\text{g}/\text{m}^3$	10%	20%	NO_2 may produce a positive bias; may be eliminated with HgO denuder	Koutrakis et al. (1988); Solomon et al. (1988)
Teflon Filter/IC	Nitrate	0.04 $\mu\text{g}/\text{m}^3$	10%	20%	Some negative interference	Koutrakis et al. (1998); Solomon et al. (1998); Hering et al. (1988)
Teflon Filter/XRF	Twenty Elements	0.5-2.5 ng/m^3	see list of elements in note #2	10%-20%	Accuracy may vary with filter loading and particle composition	Watson et al. (1997)
Quartz Filter/Thermal Analysis	Elemental Carbon	0.12 $\mu\text{g}/\text{m}^3$	5-10%	Not possible to quantify		Chow et al. (1993)
Quartz Filter/Thermal Analysis	Organic Carbon	0.12 $\mu\text{g}/\text{m}^3$	10-20%	Not possible to quantify	Converting carbon to organic carbon may introduce a positive or negative bias	Chow et al. (1993)
Beta Gauge	Mass	5 $\mu\text{g}/\text{m}^3$ for 60 minute average	10%	Not possible to quantify because there is no gold standard for particle mass	Response depends on particle composition, also loses semivolatiles during sampling	Wedding and Weigand (1993)

Table A-4. Measurements of Particulate Matter (Mass and Chemical Composition by Filter-Based and continuous In-Situ Methods) (continued)

Method	Parameter	Detection Limit	Precision	Accuracy	Interferences	References
Piezoelectric Microbalance	Mass	10 $\mu\text{g}/\text{m}^3$ for 1 minute average	10%	Not possible to quantify because there is no gold standard for particle mass	Response depends on particle composition, and loses semivolatiles during sampling	Ward and Buttry (1990)
TEOM	Mass	5 $\mu\text{g}/\text{m}^3$ for 10 minute average	10%	Not possible to quantify because there is no gold standard for particle mass	Response depends on particle composition, loses semivolatiles during sample heating	Patashnick and Ruprecht (1991)
CAMM	Mass	5 $\mu\text{g}/\text{m}^3$ for 30 minute average	10%	Not possible to quantify because there is no gold standard for particle mass	Response depends on square root of particle density	Koutrakis et al. (1995)
Chemilumin-escent Sulfur Analyzer	Sulfate	0.05 $\mu\text{g}/\text{m}^3$ for 12 minute average	5%	5%	Measures sulfur	Benner and Stedman 1990)
FPD Sulfur Analyzer	Sulfate	1 $\mu\text{g}/\text{m}^3$ for 60 minute average	5%	5%	Measures sulfur	Huntzicker et al. (1978)
Thermal/Optical Carbon Analyzer	OC/EC	0.2 $\mu\text{g}/\text{m}^3$ for 120 minute average	10%	Not possible to quantify	Measures carbon from which the organic carbon compound mass is estimated	Turpin and Huntzicker (1991)
Aethalometer	EC	10 for 1 minute average	5%	Not possible to quantify	Measures light absorption	Hansen and Rosen (1990)
ADI automated nitrate monitor	Nitrate	0.7 $\mu\text{g}/\text{m}^3$	0.2 $\mu\text{g}/\text{m}^3$	NA		Hering and Stolzenburg (1998)

Notes: #1. For all filter based methods we have assumed a flow rate of 16.67 liters/minute and a sampling duration of 24 hours. The particle sampler can be the FRM, IMPROVE, Harvard Impactor or any other PM2.5 sampler. For fine particle collection sampler differences due to inlet geometries are negligible.

#2. The detection limits for the following elements were determined based on the assumptions of presented in note #1. Also we have assumed a 13.8 cm^2 filter deposit area for a 47mm Teflon filter. The aluminum (2.5 ng/m^3), silicon (1.4), sulfur (1.2), chlorine (1.8), potassium (1), calcium (1), titanium (0.5), vanadium (0.2), chromium (0.2), manganese(0.2), iron (0.1), nickel (0.1), copper (0.1), zinc (0.2), arsenic (0.3), selenium (0.2), bromine (0.2), cadmium (2), and lead (0.5).

measurements of particulate matter and its chemical components. Included in this table are estimates of the methods limit of detection, precision, accuracy, and potential interferences or artifacts.

A.2.1 Particle Mass

Federal Reference Method

The U.S. Environmental Protection Agency has promulgated new National Ambient Air Quality Standards for fine particulate matter (particles with aerodynamic diameter, $d_a \leq 2.5 \mu\text{m}$, PM-2.5). These new standards are in addition to those existing for PM₁₀ ($d_a \leq 10 \mu\text{m}$, fine plus coarse particles, $2.5 \leq d_a \leq 10 \mu\text{m}$). For both the PM-10 and PM-2.5 standards, the Federal Reference Method (FRM) is based on the gravimetric analysis of particles collected on filters over a period of 24 hours. Gravimetric analysis was selected because most of the particle mass data used for the epidemiological studies that found associations between mortality and morbidity outcomes and ambient particle exposures are based on this method (e.g. Dockery, et al., 1993; Ito and Thurston, 1996).

The Federal Register (1997) specifies sampler design, performance characteristics, and operational requirements of the PM_{2.5} FRM. Design specifications of FRM samplers include a modified SA-246 PM₁₀ inlet that has been previously tested and approved for PM₁₀ compliance monitoring. Sampler air enters the inlet and is drawn through the WINS impactor that is designed to remove particles with an aerodynamic diameter greater than $2.5 \mu\text{m}$ by impacting the particles on the bottom of an open-topped aluminum cylindrical container. The impacted particles are trapped at the bottom of the well on an oil-impregnated glass fiber filter. A Teflon filter is placed downstream of the WINS impactor to collect the fine particles.

FRM performance specifications require that constant volumetric flow rates (16.67 ± 0.83 LPM) be monitored and recorded continuously with the temperature and pressure of the sample air entering the inlet and near the filter. FRM samplers are required to maintain the temperature of the filter during and after the sampling within ± 5 °C of concurrent ambient temperatures, regardless of heating and cooling from direct sun

or shade during and after sampling. The objective of this specification is to minimize losses of semi-volatile particles, such as ammonium nitrate and some organic compounds. Potential FRM designs use active ventilation of the enclosure that surrounds the filter holder and WINS impactor in order to attain the temperature performance specifications.

The designated FRM hardware has been tested by the EPA in several locations around the country, including Southern California, Birmingham, Alabama, and Phoenix, among others. The tests were conducted for the following reasons: a) to ensure proper mechanical functioning of the hardware; b) to assess the precision of the instrument based on collocated multiple samplers; and c) to compare the observations against other similar instruments that have been used in prior studies (e.g., the IMPROVE sampler). However, these tests did not evaluate the accuracy of a single filter-based method for the labile and volatile substances, such as ammonium nitrate and chloride, organic species, and water, which are continually in transition between the particle and gas phases. These substances can be lost or gained by the filter during or after sampling. Therefore, as known from extensive past experience, this technology is likely to be accurate for sulfate and other stable particulate components, but is subject to potentially large sampling errors for labile substances.

A priori it is expected that the performance of the FRM will be a function of the sampling location and time of year. For instance, relatively large errors are expected at locations like Southern California and Phoenix, where nitrate and semi-volatile organics are already known to constitute a substantial portion of fine particle mass (Solomon and Moyers, 1986; Solomon et al., 1989). At eastern U.S. locations, larger errors are expected during the winter than the summer because the contribution of nitrate is larger during the winter. Considering all of these factors, a credible evaluation of the FRM ought to demonstrate the relationship between method performance and particle composition over a comprehensive range of geographic locations, as well as for different seasons of the year. To date, there are few studies underway that aim to evaluate the accuracy of the FRM and, in general, filter-based gravimetric methods (see for example, a 6-8 city evaluation of the FRM collocated with denuder/filter based samplers, sponsored by EPRI in 1997-1998; Saxena, EPRI, Palo Alto, personal communication,

1998). Extensive field and laboratory studies are required to develop a systematic understanding of the physico-chemical parameters affecting the magnitude of the artifacts for semi-volatile inorganics and organics.

At this point, it is difficult to estimate the accuracy of the FRM and other filter-based methods mainly for two reasons: a) the lack of accurate semi-volatile organic measurements; and b) the limited data base of simultaneous measurements of fine particle mass and ammonium nitrate. Although an estimate of the accuracy of the FRM mass measurement cannot be provided at this time, it can be speculated that these filter-based methods will underestimate fine particle concentrations under certain conditions (see for example, Hering et al., 1988 and follow-on special issue papers; Ding et al., 1998; Hering and Cass, 1998). The extent of this bias will depend on the concentrations mostly of ammonium nitrate and semi-volatile organic species, temperature (greater losses at higher temperatures (Hering and Cass, 1998), relative humidity, variations in their relation to the corresponding volatile species during collection, and the handling of the filters following sample collection. However, the extent of bias is not a simple function, because given the same concentrations of ammonia and nitric acid in the gas phase, the highest ammonium nitrate concentrations are observed when there are cooler temperatures (i.e., ammonium nitrate is favored); however, cooler temperatures also minimize the amount of bias or loss of nitrate from the filters. For example, while there is the greatest potential for nitrate losses during the summer months, the fraction of total nitrate (gas plus particle) in the fine particles is much less than in the fall and winter months (Solomon et al., 1988) due to the temperature dependence of the equilibrium of ammonium nitrate with nitric acid and ammonia (Russell et al., 1985). However, loss of nitrate from filters is also less during cooler conditions as found in the fall and winter months. For example, in the winter, in the San Joaquin Valley during IMS95 (Solomon et al., 1996), virtually no loss in ammonia nitrate from Teflon was observed (Watson, DRI, personal communication, 1998).

Continuous Measurements

Continuous methods for the measurement of fine particle mass would have several advantages over the current FRM method. These include: a) not requiring a sequential sampling unit to collect two to seven daily samples per week; b) not requiring both an expensive temperature/humidity-controlled weighing room and extensive labor to weigh the filters; and c) providing short-term (1-hr or less) measurements of fine particle mass concentration. Therefore, even though the capital investment and labor costs are relatively high for the implementation of the fine particle mass standard, little will be learned about the temporal variability of fine particle concentrations, except at a few sites (4-7) that are to be established through the EPA supersites program and through special studies conducted by the states (e.g., California and Texas) and industry (e.g., EPRI southeast study; Saxena, EPRI, personal communication, 1998). This temporal information is needed both for understanding ambient particle health effects and for developing sound mitigation strategies. Finally, the proposed FRM cannot provide the immediate data necessary to calculate the Air Pollution Indices (APIs). Thus, the development of equivalent continuous fine particle methods that will make it possible to obtain richer data sets and to implement cost-effective large monitoring networks.

Currently, there are several continuous instruments available for fine particle measurement, but there are serious reservations regarding the quality of data these instruments can provide. An excellent review is given by Swift (1989). For purposes of this discussion, these continuous monitors can be divided into two categories: a) those which measure properties of the particles while they remain suspended in ambient air (optical/electrical), and b) those which collect particles on a filter or similar fixed substrate.

Optical/Electrical Methods:

Optical instruments (e.g., mini-RAM instruments, nephelometers, instruments measuring the Coefficient of Haze (COH), etc.) use light absorption or scattering properties to estimate particle mass concentration. These methods are commonly

dependent on both the chemical composition and the size distribution of the particles (Charlson, et al., 1974); some methods are also dependent on temperature and relative humidity. Since particle composition and size vary significantly with time and geographic location, it is difficult to adequately characterize a useful relationship between particle mass and the extinction coefficient. The advantage of these methods is that they do not require the collection of particles on filter media. Interactions between different types of particles collected on the same filter medium and/or particle-to-gas conversions, can result in significant overestimation or underestimation of particulate mass. Obviously, this problem applies both to continuous and integrated methods that collect particles on filter media. Optical and electrical methods are described in Sections A.2.4 and A.7.3. Of those described, the most likely to be used to determine PM mass concentrations employ the differential mobility particle sizer.

Using the DMA and an optical particle counter would make it possible to measure PM mass across a broad size range of atmospheric particles (0.003 - 2.5 μm diameter). Nevertheless, even in this case, the combined optical/electrical counter still would suffer from two major shortcomings. The first shortcoming arises from the fact that these counters measure the number distribution of particles that are subsequently converted to volume distribution. To measure the mass distribution, the particle density needs to be known, which for ambient particles varies with particle composition, both temporally and spatially. However, particle density can be estimated using the epiphaniometer (Gaggeler and Baltensperger, 1989; also see McMurry et al., 1998). The second (and more severe) shortcoming is intrinsic to converting a number to a volume distribution. The number distribution of ambient particles is dominated by ultrafine particles, in the size range 0.01-1.0 μm . The coarser the particles, the smaller their number concentration becomes. However, when converting a number to volume distribution, a 1.0 μm particle weighs as much as 10^3 times a 0.1 μm particle and 10^6 times a 0.01 μm particle. Consequently, this conversion is bound to lead to severe counting errors because a low background concentration of coarse particles, which may just be within the noise of the instrument, will be converted to a significant fraction of the volume distribution. Finally, a serious disadvantage is the very high cost (about \$100,000) of the two combined optical/electrical counter instruments, which is not feasible for use in the national air

quality monitoring network. However, recent work by Ehara et al. (1996) have allowed for the determination of the mass of size-selected particles using a steady-flow mass analyzer (SFMA). Thus, following the DMA or the OPC with a SFMA will allow for the determination of fine particle mass without the above two disadvantages; albeit, the method would still be expensive. Knowing the mass and the size distribution of the particles, it is also possible to determine particle density as a function of particle size (McMurry, 1998a).

Filter/Substrate-Based Methods:

There are several filter-based methods for obtaining aerosol mass on a near real-time continuous basis (typically hour averages, but shorter averages can be obtained, however, precision will likely be poorer.) These methods include the beta attenuation monitor, Piezoelectric microbalance, the Tapered Element Oscillating Microbalance, and a method based on pressure drop across a fibrous filter. These methods are described below.

The beta attenuation monitor determines aerosol mass loadings by measuring the change in intensity of beta rays passing through a membrane filter as the particles are being collected on the filter (Macias and Husar, 1976). The intensity of the beta rays passing through the filter collection medium decreases proportionally with the particle mass loading. A continuous filter tape is used in this automatic sampler, providing a “fresh” filter segment for each measurement. Initially, the beta attenuation is measured through an unexposed filter segment as a blank attenuation. The filter segment then can be exposed to ambient particles for a specified time period for particle accumulation. The beta attenuation measurement is then repeated and the mass concentration is converted after the blank correction (Wedding, 1993). Although this method has the capability, in principle, of reporting hourly average measurements, two- to four-hour averaging periods are needed to obtain enough deposits for accurate measurements at typical ambient particle mass concentrations (Chow, 1995). Also, the relationship between mass and energy absorption depends to some extent on particle composition. In

addition, a radioactive material is required as a source of beta rays adding a potential safety hazard to this method.

The Piezoelectric microbalance, which also collects particles on a substrate, was once considered a perfect way to measure particle mass loadings continuously. Particles are impacted or precipitated onto a piezoelectric quartz crystal disk surface and the decrease of the natural resonate frequency of the quartz disk is directly proportional to the particle mass on the disk, after comparison with a clean reference crystal (Olin and Sem, 1971; Ward, 1990). Although such instruments have been used with some success in providing direct readings of aerosol mass concentrations, they suffer from several limitations. These include saturation effects on the crystal surface, as well as variable particle collection efficiencies. Several investigators (Daley and Lundgren, 1975; Lundgren, 1977) found that the frequency change for a given incremental mass deposit on the sensor does not remain constant as the sensor becomes loaded. This is due to the change in the particle collection patterns over time. Some particles, such as CaCO_3 , deposit uniformly in the beginning but, as the loading increases, the freshly-deposited particles tend to accumulate near the center of the sensor, presumably because of the change in the electrical conductivity of the collection surface. Other types of aerosols, such as Fe_2O_3 , tend to deposit less uniformly than expected after initial particle deposition on the crystal. As a result, the incremental decrease in frequency of a particle laden crystal is not the same as that of a fresh crystal, causing a potential bias for the particle mass concentration measurement. In the research of Lundgren 1977, the response of the instrument became non-linear within a few minutes after beginning the experiments when tested with black carbon particles.

The Tapered Element Oscillating Microbalance (TEOM) has been widely used as a continuous PM_{10} mass measurement monitor (Pataschnick and Rupprecht, 1991) and by replacing the PM_{10} inlet with a $\text{PM}_{2.5}$ inlet has been used to measure $\text{PM}_{2.5}$ mass concentrations continuously. With this method, particles are continuously collected on a filter mounted on the tip of a glass element that oscillates in an applied electric field. The oscillation frequency of the glass element decreases as the mass of the particles collected on the filter increases. This is a sensitive method with a typical time resolution of five minutes. To maintain the necessary precision, the tapered element must be kept at a

constant temperature to minimize effects of thermal expansion and contraction, and at an elevated temperature to remove adsorbed water, to prevent artifacts due to variation in ambient humidity. For these reasons, the sample chamber and inlet air are normally heated to 50 °C. As a result, there can be significant losses of semi-volatile organic and inorganic constituents, which typically represent a large fraction of the total mass (Allen, et al., 1997). This problem is more pronounced for PM_{2.5}, because this size range typically has a greater fraction of unstable compounds (ammonium nitrate and semi-volatile organic compounds) than does PM₁₀. In addition, as the composition of the air sample changes, the partitioning of air pollutants between the gas and particle phase changes. Therefore, adsorption and/or desorption of gaseous species can take place on the filter. This gain or loss of mass on the filter is a serious problem, not just with the TEOM, but with any method that collects particles on a filter over a prolonged period of time. To help overcome the problems associated with heating the inlet several groups are working on the design of systems that operate with controlled relative humidity (Rupprecht, 1998; Edgerton, 1998).

Recently, a continuous fine particle mass sampler that can provide 20-minute measurements was developed (Koutrakis et al., 1995). This method is based on the continuous measurement of pressure drop across a fibrous filter (Fluoropore) during particle sampling. The performance of this particle mass monitor has been validated through laboratory and preliminary field tests. A filter tape transportation system allows for unassisted particle sampling for several weeks. For each sampling period, a new segment of the filter tape is exposed. This method combines measurement at ambient temperatures, short sampling periods, and low face velocity, which, together, result in minimum volatilization or adsorption artifacts. In addition, because this technique requires a low flow rate (0.3 liters/min), the relative humidity of the air sample can be controlled to 40% or less by passing the air sample through a Nafion diffusion dryer prior to its collection. This is in accordance with the FRM, which requires that particle filter samples be conditioned prior to weighing at a relative humidity of 40% to remove particle-bound water. These are important features necessary for accurate aerosol measurements relative to the FRM, which are not easily achievable with previous methods. Although this pressure drop method looks promising, more field investigations

are necessary to validate it for ambient air sampling for a variety of geographic locations and seasons (i.e., different chemical atmospheres).

Summary:

There is a great need for the development of accurate, continuous particle mass monitors. As long as health effects studies cannot identify the chemical constituents or physical properties of particulate matter that are responsible for the observed morbidity and mortality, the total mass of all ambient particle components should be the criterion for particle measurement. Continuous mass monitoring methods need to be robust for both stable species (e.g., sulfates and dust) as well as labile species (e.g., SVOCs, ammonium nitrate and ammonium chloride). Furthermore, the effects of relative humidity and temperature on particle mass measurement also need to be addressed. For example, for comparison to the FRM, sampled particles should be conditioned to 40% RH (when ambient RH exceeds 40%) to minimize the effect of variations in the water associated with particles. The air sample should not be heated because semi-volatile compounds will volatilize, resulting in an underestimation of particle mass. *In situ* aerosol measurements are necessary to minimize positive or negative particle mass sampling artifacts. If a filter medium is used, the collection surface should not be used for more than one hour to minimize these artifacts. To maintain the gas/particle equilibrium, the continuous method should either regenerate the collection surface or use a new surface for each sampling interval. Finally, none of the existing continuous monitors can provide mass measurements equivalent to those of the FRM. Considering that the ability of the FRM and most of the filter-based methods in general to meet these criteria are questionable (i.e., artifact free mass concentrations), as mentioned above, a serious problem is posed that needs to be addressed in the years to come.

A.2.2 Particulate Matter Chemical Composition

This section first describes several methods for determining the chemical composition, and often size of single atmospheric particles. Next, measurement methods

for the determination of specific chemical compounds in bulk time-integrated samples are described, including appropriate laboratory chemical analysis methods. The bulk field collection and laboratory methods are summarized in the critical review by Chow (1995). Continuous chemically specific methods are also described for each species discussed below. The latter, as well as the continuous single particle measurements, represent the state-of-the-science in determining components of atmospheric aerosols.

Measurements of Single Particles

Time-Integrated Measurements:

Electron microscopy of single particles collected on grids is the only available technique that can provide particle composition and morphology information simultaneously; although it is not in real-time or continuous (Fletcher and Small, 1993). The combination of scanning electron microscopy and energy analysis of emitted x-rays is the most powerful tool for detailed information about shape and chemistry of single particles. Elemental analysis for elements heavier than sodium is possible. The major limitation of electron microscopy is the extreme amount of labor required to obtain statistically significant data, though semi-automated analysis schemes are available (Anderson et al, 1988; Artaxo et al, 1992). Because high vacuum is conventionally required for analysis, detection of volatile and semi-volatile components is difficult. New techniques have attempted to increase analysis pressure above 5 torr to reduce such losses (Danliatos ,1988). Selection of collection grids is also critical, with carbon or copper typically chosen as appropriate to minimize background interference with elements of interest (Huang and Turpin, 1996). Although composition information is labor intensive and often difficult to quantify, the unique combination of morphology and composition make electron microscopy the ideal tool for resolving external mixtures of particles, for example, mixed salt (McInnes et al, 1994) or carbonaceous particles. Collector grids are easy to operate and add to existing sampling protocols.

Continuous Measurements:

One of the most significant advances of the last decade has been the development of methods to measure the chemical composition of single particles in-situ in real-time, thus providing important information for characterizing atmospheric aerosols. These methods are summarized in Table A-5. Any chemical/microphysical aerosol model includes external and internal mixtures of particles with complex chemical composition that can only be resolved observationally by detecting single atmospheric particles.

Such atmospheric detection has been demonstrated using laser vaporization of particles larger than about 0.1 to 10 μm diameters (McKeown et al., 1991; Thomson and Murphy, 1993; Prather et al., 1994; Hinz et al., 1996, Noble and Prather, 1996; Johnston and Wexler, 1995). Particles are detected by laser light scattering which then triggers a high powered UV pulsed laser which vaporizes the particle in a plasma that creates molecular and atomic ions that are then analyzed with a time-of-flight (TOF) mass spectrometer. Sensitivity to trace chemical composition in particles as small as 0.1 μm is very good. The accuracy for chemical speciation is harder to quantify. For example, analysis of organic compounds tends to be equivalent to elemental carbon analysis. Overall, sensitivity is also difficult to quantify since sampling efficiencies are size dependent and not yet well characterized. Efforts to characterize sampling efficiency for the ATOFMS are underway through a study at the University of California, Riverside (Prather, UCR; Cass, Caltech, personal communications, 1998). They are obtaining size-resolved chemical characterization of aerosols using a MOUDI as well as size distributions by some of the methods discussed above. The size and chemically resolved impactor data provide a calibration measure for the chemical composition data collected by the ATOFMS.

Aerodynamic particle size can be determined by passing particles through two scattering lasers as in the aerodynamic particle sizer (Prather et al., 1994; Noble and Prather, 1996). Other groups have extended measurements to ultrafine particles by randomly firing the vaporization laser (Reents et al., 1995), including using a DMA to size selected particles (Carson et al., 1997). Despite current limitations on accuracy, field observations to date have clearly indicated the potential of such single particle analysis in

Table A-5. Measurements of Particulate Matter Particle (Single Particles Analyzers)

Method	Variable Measured	Limit of Detection	Precision	Accuracy	Potential Interferences/Artifacts	References
Laser Vaporization Mass Spectrometry	size-resolved single particle composition	$0.1 < d < 5 \mu\text{m}$	fair	poor/fair	sampling bias toward larger particles ($>0.5 \mu\text{m}$)	Noble et al., 1994; 1996, Prather et al., 1994
Aerosol Mass Spectrometer	size-resolved single particle composition		fair	fair	limited to volatile and semi-volatile components	Jayne et al., 1997

resolving external mixtures of sulfate and nitrate particles (Murphy and Thomson, 1997), detecting seasalt in sulfate particles aloft (Middlebrook et al., 1997), identifying particle source categories via chemical tracers (Hinz et al., 1996) and tracing the transport of pyrotechnically-derived particles following fireworks (Liu et al., 1997).

A variant of single particle mass spectrometry is an aerosol mass spectrometer (AMS) based on thermal vaporization of single particles (Jayne et al, 1997) sampled with an aerodynamic inlet that focuses particles into a beam coupled to a vacuum chamber (Liu et al., 1995). Following aerodynamic particle sizing using mechanical TOF chopping, particles are vaporized and then detected with a quadrupole molecular mass spectrometer. Particle sizes spanning the range of ultrafine to coarse can be quantitatively analyzed. Although sensitivity is significantly less than for the laser based analyzers and detection is limited to volatile and semi-volatile chemical components, the AMS has the potential to provide a robust, size-resolved real-time aerosol chemical analyzer. AMS instrumentation is based on vacuum and mass spectrometric technology, utilizing no lasers.

The power of single particle analysis has been best demonstrated in the recent study of the conversion of seasalt aerosol from NaCl to NaNO₃ as marine air passed over the Los Angeles coast (Gard et al., 1998). That study represents the paradigm for intensive field programs of aerosol chemistry. While the single particle observations provided the most dramatic evidence for chemical transformation of atmospheric aerosols, overall aerosol microphysics and size/chemical distributions were monitored with a number of ancillary measurement techniques that served to calibrate the single particle measurements.

Sulfate (and related particle strong acidity)

Time-Integrated Measurements:

Sulfate is one of the most robust species to measure particulate matter because it remains stable during and after sample collection. Most of the existing data are of great accuracy except those collected using glass fiber filters, which have a positive artifact

caused by reaction of the filter material with sulfur dioxide. Sulfate is commonly collected on Teflon or quartz fiber filters (Chow, 1995). Aqueous extracts of these filters have usually been analyzed using ion chromatography (and less frequently, using spectrophotometric methods). In general, sulfate data have an accuracy of about 5%, which is typically independent of the sampling method, location and season. Furthermore, measurements of ammonium ion associated with sulfate, such as ammonium sulfate, letovicite or ammonium bisulfate, have a similar accuracy. Total particulate sulfur also is routinely analyzed using X-Ray fluorescence (XRF). Measurements of collocated samples by ion chromatography and XRF are usually highly correlated. The typical mass ratio of (sulfate by IC)/(sulfur by XRF) is about 3, which indicates that almost all of the fine particle sulfur is in the form of sulfate.

Particle strong acidity (hydrogen ion), is mostly associated with sulfates species. Denuder/filter pack techniques have been used to measure particle acidity and other ionic species (Koutrakis, et al., 1988). The samples consist of three components: a) a PM_{2.5} inertial impactor to remove coarse particles (which are generally alkaline and would consequently neutralize the fine particle strong acidity collected on the sample filter); b) a diffusion denuder to remove gaseous ammonia from the air sample; and c) a Teflon filter to collect fine particles. The fine particles are subsequently extracted using an aqueous solution of dilute perchloric acid. The hydrogen ion concentration is measured using a pH meter equipped with a semi-microelectrode. Although the accuracy of hydrogen ion measurements (about 10%) is less than that of the related ionic species, sulfate and ammonium (about 5%), their accuracy is considerably better than those of carbonaceous aerosols and nitrate (about 15%). The ionic balance, $[\text{ammonium} + \text{hydrogen}] / [2 \times [\text{sulfate}]]$, is close to unity during acid aerosol episodes, confirming the accuracy of the hydrogen ion measurements. Note that during these episodes no significant amount of particle nitrate is present because ammonia has been depleted by reaction with excess acidic sulfate.

Continuous Measurements:

Continuous monitoring of particle sulfate is possible using the flame ionization method developed by Huntzicker, et al. (1978). According to this method sulfur species are combusted in a hydrogen flame to create excited sulfur dimers. The intensity of the fluorescence emission is proportional to square of the particulate sulfur concentration. Using a denuder to remove sulfur dioxide and thermal ramping this continuous monitor provides separate measurements of sulfuric acid, ammonium sulfate and bisulfate and, non-volatile sulfate. Doping the hydrogen with sulfur hexafluoride improves the sensitivity and yields a nearly linear response (Appel et al., 1989). An intercomparison between this method and conventional filter samples analyzed by ion chromatography showed good agreement (Suh et al., 1994). Sulfate can also be measured using a chemiluminescence analyzer (Benner and Stedman, 1989). According to this method, particulate sulfur species are converted to SO in a hydrogen flame. Subsequently, SO reacts with O₃ to produce an excited state of SO₂. Similarly to the flame ionization method, described above, a denuder is used to remove sulfur dioxide. Thermal ramping with this monitor also can provide the same sulfate speciation as the flame ionization method. Finally, it should be mentioned that both continuous methods assume that all particulate sulfur is present in the form of sulfate. This assumption is generally true for typical ambient atmospheres.

Sulfate can also be monitored continuously using annular denuders or wet denuders followed by a steam chamber to form condensation nuclei that are subsequently collected and analyzed in near-real time by ion chromatography. This method can also be used to measure other anions and cations, as well as their gas-phase counterparts (Ito et al., 1998; see the review by Dasgupta, 1993; Simon and Dasgupta, 1995; Wyers et al., 1993).

Nitrate

Time-Integrated Measurements:

A variety of filter media have been used to collect particulate nitrates, including: Teflon filters, glass fiber filters, sodium carbonate-coated glass fiber and nylon filters. Aqueous extracts of these filter media were analyzed mostly by ion chromatography or colorimetric methods to determine the nitrate concentration. Accurate measurements of nitrate require the removal of gas phase nitric acid prior to particle collection and the collection of nitrate on a filter medium which binds any nitric acid vapor produced by volatilization of the collected particulate ammonium nitrate, such as sodium carbonate-coated glass fiber or nylon filters. Removal of the gaseous nitric acid can be achieved by using diffusion denuders, typically coated with Na_2CO_3 or MgO (Koutrakis, et al., 1995; Solomon et al., 1988) or (unanodized) aluminum inlets (John et al., 1988). Previous methods that have used Teflon, glass fiber, or quartz fiber filters are negatively biased due to volatilization of ammonium nitrate during and after sampling (Dunwoody, 1986; Witz, et al., 1990; Solomon et al., 1988; also see Hering et al., 1988 and other related special issue articles). The equilibrium between particle ammonium nitrate, gaseous ammonia and nitric acid can be perturbed by changes in relative humidity and temperatures. Losses of ammonium nitrate can also be caused by the presence of ammonium bisulfate and similar incompletely neutralized forms of sulfuric acid collected on the filter media (Koutrakis et al 1992). To date, there is no agreement among the different studies regarding the extent of nitrate loss. This disagreement stems from the fact that these results correspond to a variety of locations, meteorological conditions, and sampling methods. A recent study by Hering and Cass (submitted to *J. Air Waste Manage. Assoc.*) presents a model that can be used to estimate nitrate losses. This may become an excellent tool to estimate corrections for particulate nitrate data from previous and future studies.

Nitrate is one of the fine particle constituents that will be measured as part of the fine particle speciation network that the U.S. EPA is planning to initiate. The proposed sampler will be similar to the FRM sampler described above, but will be equipped with a

denuder to remove HNO_3 followed by a nylon filter to collect fine particle nitrate free from artifacts. Nylon filters are slightly alkaline and can collect nitrate quantitatively. However, there is some evidence that a small amount of nitrogen dioxide can be collected by these filters (Preliminary results obtained during the Harvard/EPRI methods validation studies). A small fraction of ambient nitrogen dioxide is initially retained in the form of nitrite and is converted slowly to nitrate by ozone or other atmospheric oxidants that are present in the air sample. This positive bias may be about 5-15% at sites with high nitrogen dioxide concentrations. Future studies are needed to investigate this artifact.

Nitrate, as well as other semi-volatile compounds, can be lost after sampling during shipping and storage. Witz et al. (1990) found that a large fraction of nitrate and ammonium (greater than 50%) was lost from glass- and quartz-fiber filters that were stored in unsealed containers. These containers were stored for a period of two to four weeks prior to analysis. Therefore, the use of sealed containers maintained at reduced temperatures during shipping and storage is necessary to minimize these losses.

Continuous Measurements:

The Automated Nitrate Monitor is a new method that provides automated measurement of airborne particle nitrate concentrations with a time resolution of ten minutes (Hering and Stolzenburg, 1998). The method uses an integrated collection and vaporization cell whereby particles are collected by a humidified impaction process, and analyzed in place by flash vaporization. The system operates continuously, unattended, yielding 144 measurements per day, each corresponding to an eight-minute sample collection followed by a 90-sec analysis. Operations are unattended apart from twice-weekly calibration checks. Preliminary results are available immediately.

The approach is similar to the manual method that has been used for over twenty years to measure the size distribution of sulfate aerosols (Hering and Friedlander, 1982). In this case, however, the particle collection and analysis have been combined into a single cell, allowing the system to be automated. Particles are humidified prior to impaction to eliminate the rebound of particles from the impaction surface without the use of grease (Winkler, 1974; Stein et al., 1994). Interference from vapors such as nitric

acid is minimized by use of a denuder upstream of the humidifier. Analysis is done by flash-vaporization into a nitrogen carrier gas with quantitation by a chemiluminescence NO_x analyzer, similar to that described by Yamamota and Kousaka (1992) and described in Section A.1.1 of this report. The flow system is configured such that there are no valves on the aerosol sampling line. Field validation procedures include on-line checks of particle collection efficiency, calibration with aqueous standards applied directly to the collection substrate, and determination of blanks by measurements of filtered, ambient air.

The method has been compared to 10-min data for total fine particle concentrations as indicated by nephelometry, and to 6 to 24 hour nitrate concentrations measured by denuded filter methods. For measurements in Denver Colorado (NFRAQS) and in Riverside (SCOS'97) the 10-minute changes in fine particle nitrate tracked the 10-minute changes in particle scattering. For the initial measurements in Denver, some discrepancies were found with the filter measurements. However, for Riverside, comparison with 14 days of 24-hr denuder-filter sampling gives a correlation coefficient squared of $R^2=0.87$, and shows no significant bias (i.e., the regression slope is not significantly different from 1) (Saxena, private communication, 1998). As currently configured, the system has a detection limit of $0.7 \mu\text{g}/\text{m}^3$, and a precision of $0.2 \mu\text{g}/\text{m}^3$. Field operations with the system in Riverside showed that it was robust, providing nearly uninterrupted data over the six-week study period.

As described under sulfate, particle nitrate also can be determined continuously, in near-real time using a combination of annular or wet denuders coupled to an ion chromatographic system.

Ammonium

Time- Integrated Methods:

Particles collected on Teflon filters are extracted using an aqueous solution. Ammonium ion can be analyzed using ion chromatography (IC) or colorimetric methods. Although ion chromatography is more expensive and more labor intensive, it has become

the method of choice, because of its versatility and accuracy. For instance, ion chromatography can be used to measure other important cations, such as sodium and potassium and anions such as nitrate, sulfate and chloride; although separate IC columns are needed to measure both cations and anions. Colorimetric methods can only measure one species at a time. Because ammonium sulfate salts are very stable, negligible loss occurs during sample collection and storage. However, ammonium nitrate, which is an important constituent of fine particle mass, is unstable and can volatilize during both sample collection and storage. The extent of volatilization depends on many parameters, including temperature and relative humidity. The dissociation of ammonium nitrate results in the formation of gas phase ammonia and nitric acid. As mentioned above, a nylon membrane or sodium carbonate-coated filter is used to trap the nitric acid lost from the Teflon filter. Since no collection medium is used for the volatilized ammonia, one would expect that current sampling techniques underestimate ammonium concentrations due to volatilization of ammonium nitrate. It is worth mentioning that fine particle mass contains many acidic compounds. Consequently, a fraction of volatilized ammonium (in the form of ammonia gas) can be retained on the Teflon filter by reacting with the acidic compounds; however, this has never been quantified. This mechanism can reduce underestimation of collected ammonium ion caused by volatilization.

Continuous Measurements:

A semi-continuous measurement method was recently developed by Ito et al, 1998. According to this method particles are collected in a small mist chamber. Similar methods have been used for the measurement of related acidic gas-phase and particle species (see the review by Dasgupta, 1993; Simon and Dasgupta, 1995; and discussed previously under sulfate). Subsequently, the dissolved ionic species (including ammonium) are analyzed by an on-line ion chromatograph. This method can provide short-term measurements (thirty to sixty minutes). While the method is accurate and sensitive, the instrument is bulky and requires wet chemistry in the field.

Chloride

Time-Integrated Methods and Continuous Measurements:

Aqueous extracts of Teflon filters can be analyzed using ion chromatography to determine chloride concentrations as described above under continuous methods for ammonium. Although chloride can be an important constituent of fine particulate matter in coastal environments, to date only a few studies have measured this species (see for example, Solomon et al., 1988a; 1989; Eldering et al., 1991). One reason for this is that many precautions must be taken during filter preparation, sampling, transport and analysis to minimize chloride contamination of the samples. High and variable blanks for both laboratory and field can cause sample values to be merely qualitative. A method to continuously measure chloride has not been reported to date, however, the continuous denuder/IC methods described above for sulfate and ammonium could be used for chloride measurements, if appropriate precautions are made to assure that blank values are low.

Elements

Time-Integrated Measurements:

Elemental analysis of aerosol samples is important because it can be helpful in identifying particle sources. To date several analytical methods have been used to determine the elemental composition the particulate matter. These methods include: of X-Ray Fluorescence (XRF), Proton Induced X-Ray Emission (PIXE), Instrumental Neutron Activation Analysis (INAA), Atomic Emission Spectrophotometry (AES), Inductively Coupled Plasma (ICP) equipped with atomic emission (ICP-AES) or mass spectroscopy (ICP-MS). From these methods XRF and PIXE are the most widely used because they require no sample preparation. In contrast, both AES and ICP methods require filter extraction of the filter sample using strong acidic solutions to achieve sample dissolution. However, because ambient particles are complex it is difficult to

dissolve them completely, regardless the strength of the solvent, thus reducing the accuracy of the analysis. Also, extraction is a time consuming and expensive. Nonetheless, AES is used occasionally for the analysis of sodium and magnesium, which cannot be analyzed by either XRF or PIXE methods. ICP-AES and ICP-MS can be used to analyze a large spectrum of elements with detection limits suitable for aerosol samples. However, as with AES, these methods require sample extraction and are destructive. ICP-MS can also be used for isotope analysis. Although INAA is a non destructive method, the sample must be folded and sealed in plastic. Because the sample is bombarded by gamma rays it becomes radioactive. Of course this makes it difficult to use the sample for further analysis. Finally, INAA cannot be used for the analysis of certain important elements, including sulfur, lead, and silicon; however, it is extremely sensitive for many trace metals, especially the rare earth elements.

XRF (Dzubay and Stevens, 1975; Jaklevic et al., 1977) and PIXE (Cahill et al., 1990) have been used extensively in the analysis of ambient aerosols because they are non-destructive, have multi-element capabilities, and have relatively low cost. These methods are usually performed on Teflon filters for approximately forty elements (from sodium to uranium). However, for typical atmospheres the analysis is meaningful only for half of these elements, including aluminum, silicon, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, nickel, copper, zinc, arsenic, selenium, bromine, cadmium, and lead. The sensitivity of these methods is on the order of few ng/m^3 for twenty four-hour samples (flow rates of 10-20 liters per minute). Because these detection limits are quite low, XRF and PIXE analysis provide meaningful information for typical samples. Nonetheless, quite often environmental samples have elemental measurements that are below the detection limit of the methods. Thus analytical uncertainties can have a significant impact on the quality of the data analysis such as for source apportionment studies. Since particle concentrations are expected to decrease due to the implementation of the new PM NAAQS, XRF and PIXE may not be sensitive enough. Finally, it should be mentioned that during the analysis using these methods, the sample is introduced into a chamber that is evacuated and the sample is slightly heated due to the absorption of X-rays or protons. As a result, species that can volatilize such as ammonium nitrate and certain organic compounds can be lost during

the analysis. This is overcome, however, by using atmospheric pressure energy dispersive XRF using secondary ions as the excitation source. In these systems, air is replaced with He while maintaining atmospheric pressure, and sample heating by direct X-ray methods is eliminated due to the use of secondary ions as the excitation source.

Continuous Measurements:

To date there are no continuous measurement techniques for the quantitative elemental analysis of ambient aerosols. Currently, some research efforts are under way, (Ondov, University of Maryland, personal communication, 1998), but it will take at least one to three years before new monitoring techniques will appear. These techniques will be useful for generating the quality of data sets needed for more comprehensive source apportionment studies.

Carbonaceous Compounds

Time-Integrated Measurements:

There are three types of carbonaceous particles:

Organic carbon that can be present in the form of hundreds (or more) of organic compounds such as alkanes, alkenes, mono and di-carboxylic acids, aromatic polycarboxylic acids, polyaromatic hydrocarbons, ketones, quinones, nitrogen containing compounds, etc. These compounds do not absorb light in the visible region, and a large fraction of them can be present in both the particle and gaseous phases (semi-volatile species).

Elemental carbon or (visible) light absorbing carbon.

Carbonate carbon, which is in the form of calcium carbonate or other salts.

Several methods have been employed to separate or measure independently the concentrations of elemental carbon and organic carbon in atmospheric particles: thermal analysis, digestion, extraction, optical methods, photoacoustic methods. Of these, thermal analysis, optical methods, and photoacoustic spectroscopy are used most often today. These methods are discussed in detail by Wolff and Klimisch (1982), Cadle et al. (1983), and Yasa et al. (1979).

The collection of carbonaceous particles is still an area of considerable controversy. One simple method that has been widely used is to collect total carbon on a series of two quartz filters. Presumably, the first collects all of the particle phase carbon (elemental and organic) and a small fraction of gas-phase organic carbon. Likewise, the second quartz filter is supposed to collect only the same small fraction of gas-phase organic carbon as collected by the first filter. Therefore, the concentration or particle phase organic carbon is calculated by subtracting the amount of organic carbon on the second from that on the first stage. However, this assumption does not take into account particle phase organic carbon that can volatilize from the first filter and be collected by the second quartz filter. When this volatilization occurs, it results in underestimation of particle phase organic carbon, similar to the situation with the collection of particulate ammonium and nitrate on filters described above.

The two-quartz filter approach has been used by the IMPROVE network for the determination of organic and elemental carbon. Because the accuracy of this method is questionable, as described above, more research is needed prior to its implementation. Eatough et al. (1989) and Tang et al. (1994) concluded that desorption of organic gases from particles on the first quartz filter was the dominant sampling artifact (negative artifact), while Turpin et al. (1994) suggested that organic gases can be collected by the quartz filter (positive artifact). Turpin et al. found that adsorbed organic gases represent 10 to 40% of the organic carbon measured on quartz filters in southern California. This study suggested that: a) organic gas absorption (positive bias) was much larger than organic particle volatilization (negative bias); b) as sample durations increase the fraction of the adsorption bias decreases because the adsorbed gases reach equilibrium with the collected particles and the filter becomes saturated; and c) the magnitude of the bias depends on the composition of the organic gases and particles present in the air sample.

For these reasons, the US EPA national speciation network is suggesting the use of denuders (carbon or XAD-2 coated) to remove semi-volatile organic species and reactive organic gases that might absorb on a quartz filter (EPA, 1998). However, additional testing and evaluation of the denuder/filter method system is needed (Turpin, 1998).

There is a great need to develop bias-free particle organic carbon sampling techniques. The diffusion denuder approach may be a sound approach to overcome the problems mentioned above. According to this sampling technique, gaseous organic compounds are removed using an activated carbon diffusion denuder or an XAD-2 coated denuder. Subsequently, the particle-phase organic carbon can be collected downstream of the denuder using a series of two-quartz filters or a quartz filter followed by a PUF cartridge. The first filter collects particle phase organic carbon, while the second quartz filter or PUF cartridge collects the organic carbon volatilized from the first quartz filter. The total particle carbon concentration is determined by adding the concentrations of the first and second filter or PUF cartridge, respectively. To achieve maximum accuracy, the denuder must collect close to 100% of all gas phase organic compounds, and the second filter must collect all of the volatilized organics coming off of the first filter. Multi-channel activated carbon denuder or XAD-coated denuder systems also have great potential, but they need to be developed and tested further.

Elemental carbon can be determined by optical methods, by thermal analysis, and by photoacoustic spectroscopy. Optically, elemental carbon is determined by measuring the absorption or reduction in transmittance of light passed through a particle-laden Teflon or quartz filter, such as in the integrating plate method (Lin et al., 1973). Today, thermal methods, which use temperature to separate organic carbon from elemental carbon, are combined with optical methods, where either light reflectance (TOR), or light transmission (or absorption, TOA) is measured and used to compensate for charring of organic carbon during the last thermal OC temperature step. However, their results differ depending upon the specific organic composition of the collected particles. All thermal methods measure carbon (usually as methane) and thus have to multiply the carbon concentration by an average factor of 1.4 to estimate total organic compound mass concentrations. This factor comes from an old study and is expected to vary with location and season and usually may be higher than 1.4 as discussed by Andrews et al.

(1998). Therefore, organic compound concentrations may be higher than those reported by previous studies. Photoacoustic spectroscopy deduces the elemental carbon concentration from light absorption by measuring the sound generated due to heating of the sample by laser light (Adams et al., 1990; Turpin et al., 1990a; Arnott et al., 1998b). Good agreement has been shown (within 15%) between a light absorption filter technique and photoacoustic spectroscopy (Foot and Kilsby, 1989) and the thermal-optical method and photoacoustic spectroscopy (Turpin et al., 1990). All three methods for determining elemental carbon are described in more detail below under continuous methods.

Organic compounds can represent a large fraction of fine particle mass (e.g., Gray et al., 1984; Solomon et al., 1986; 1989). Also organic compound speciation can provide a great deal of information regarding the sources and formation processes of carbonaceous particles (Schauer et al., 1996). Although speciation is desirable, it is not easy to perform because there is no single analytical method that can be used to analyze all classes of organics. Usually, non-polar organics are analyzed using thermal desorption or solvent extraction followed by gas chromatography (GC) and mass spectrometry (MS) (Mazurek et al., 1987; Mazurek et al., 1993; Schauer et al., 1996). Analysis of polar organic compounds is more challenging because special sample preparation is required (e.g. derivatization) for the different compound classes (Blando et al., 1998). Comprehensive determination of organic speciation is expensive and yields a large data set that may be time consuming to process and incorporate into air quality models. It may be more cost-effective to develop inexpensive methods that allow the measurement of specific characteristic groups of organic compounds (Turpin, 1998). Similar lumping approaches for VOC species have been used successfully in ozone modeling. Attempting to obtain a comprehensive spatial and temporal patterns on hundreds of organic compounds may not be a sound strategy. On the other hand, organic aerosol speciation has provided an extensive new set of tracers for receptor-type modeling and has allowed for the apportionment of many more sources to PM at receptors than would occur using just the major species and existing inorganic tracers (e.g., lead is no longer a suitable tracer for automobiles) (Schauer et al., 1996 and references within).

Continuous Measurements:

Elemental carbon (EC) concentrations can be estimated from light absorption measurements and photoacoustic spectroscopy. The aethalometer is the most commonly used instrument (Hansen and Rosen, 1990) for determining light absorption of atmospheric particles. In this method, particles are continuously collected on a quartz-fiber filter tape. The difference in light absorption between the exposed and blank sections of the tape is assumed to be proportional to the amount of the light-absorbing particles. It is also assumed that all light absorbing material is elemental carbon and that its light absorption coefficient remains constant for different sources. However, this assumption has not yet been thoroughly validated. A few studies have shown a good agreement between aethalometer data and thermal analysis methods (Allen et al., 1997). However, more studies need to be conducted to examine the relationship of light absorption vs elemental carbon as a function of ambient aerosol composition.

An *in-situ* thermal/optical carbon analyzer has been developed by Turpin and Huntzicker (1991). In this method, particles are collected on a quartz-fiber filter. Organic carbon is then volatilized by heating the filter at 650°C in a helium atmosphere. This volatilized organic carbon is then converted to carbon dioxide, which is subsequently reduced to methane, which is measured using a flame ionization detector as mentioned earlier. Elemental carbon is measured by lowering the temperature to 350°C in the presence of oxygen. The evolved carbon dioxide is reduced to methane and is measured by the flame ionization detector. During volatilization of the organic carbon, light transmission through the filter is measured to make a correction for charring that is caused by pyrolysis of the high temperature organic species. Finally, an identical quartz filter is placed downstream in order to take account collection of gas phase organic carbon by the first quartz filter.

A continuous organic/elemental carbon has been developed (Turpin et al., 1990) and a similar instrument is available commercially. In these methods, aerosol is either collected on a filter (Turpin et al., 1990) or particles are collected on an impaction surface (Rupprecht & Patashnick). Subsequently, the surface is heated at two different temperatures in order to measure the concentration of organic and elemental carbon.

Although this method can provide information about the temporal variability of carbon concentrations, the accuracy is questionable for two reasons: a) they only collect particles above $0.15\ \mu\text{m}$, which can result in a negative bias because a large fraction of particles containing carbon can have a diameter below this size; and b) during the thermal ramping organic carbon can be pyrolyzed, which can result in a negative bias for organic carbon and in a positive bias for elemental carbon. Unlike the thermal optical method, charring is not corrected and the extent of these biases will depend on the composition of the carbonaceous particles.

Photoacoustic spectroscopy is based on the photoacoustic effect (Pao, 1977; Rosencwaig, 1980). In this method, radiation from a laser beam is absorbed by the sample and transferred as heat energy to the surrounding gas, which creates an increase in pressure in the sample cell. By modulating the laser, the oscillating pressure forms a sound wave that is detected with a microphone. The microphone signal is directly proportional to the optical absorption. The lower limit of detection for light absorption is $0.4\ \text{Mm}^{-1}$, which corresponds to an elemental carbon mass density of about $40\ \text{ng/m}^3$, assuming a light absorbing efficiency of $10\ \text{m}^2/\text{g}$. A comparison of the photoacoustic method to the thermal/optical method has been performed (Turpin et al., 1990a and references within; Adams et al. 1990). The two methods compared well with $R^2=0.82$ and a slope statistically equal to 1. Recently, Arnott et al. (1998a) compared photoacoustic measurements of aerosol light absorption with concentrations of black and elemental carbon and obtained strong correlations ($R^2 = 0.94$ and 0.85 , respectively).

A.2.3 Gas-Phase Condensable Chemical Species

Nitric Acid and Ammonia

Time-Integrated Methods

Nitric and ammonia gases are precursors of important fine particle mass constituents such as nitrate and ammonium, respectively. Therefore, determination of the ambient concentration of these gases is important. Although different types of integrated

active and passive sampling techniques exist for these gases, the most important are those that use diffusion denuders. Denuder based sampling techniques are accurate, sensitive and relatively easy to use. Tubular, annular, honeycomb glass, or cloth denuders can be coated with sodium carbonate or citric acid to collect nitric acid or ammonia, respectively. After sampling, the denuders are extracted using an aqueous solution. Subsequently, the extract is analyzed by ion chromatography for nitrate or ammonium to determine the nitric acid or ammonia concentration, respectively. For collection rates ranging between 10 and 20 liters per minute and sample durations of twenty four hours the detection limits for these methods are on the order of 1ppb (Koutrakis et al., 1988).

Denuder methods coupled to ion chromatography have been reported to measure HNO_3 and NH_3 continuously in-situ and are also capable of determining aerosol nitrate and ammonium (Dasgupta, 1993; Jongejan et al., 1997; Simon et al., 1991; Lindgren, 1992; Vecera and Dasgupta, 1991; Sorensen et al., 1994). These methods show great promise for continuous, near real-time measurements of HNO_3 , HCl , HNO_2 , and SO_2 , and their particulate phase counterparts. These systems have also been used aboard aircraft platforms (Dasgupta and Lindgren, 1989; Kok et al., 1990). However, whether used at ground-level or aboard aircraft, more thorough evaluations of these methods are needed.

A second denuder-based method uses tubular or annular denuders coated with MgO to remove acidic gases with great efficiency and capacity. Since the MgO denuder cannot be analyzed directly for the acidic gases of interest, a second reactive filter is located in parallel to collect both acidic gases and their aerosol counterparts. The difference between the two reactive filters is the gas-phase concentration of the acid species of interest (see, for example, Solomon et al., 1988; Hering et al., 1988). This method is usually referred to as the denuder difference method. The reactive backup filter, typically, is pre-washed nylon when using a MgO coated denuder; however, fibrous filters impregnated with Na_2CO_3 or KOH can also be used, but then the denuder should be coated with these bases to provide consistency with the reactive filters. Nylon is best used only for HNO_3 due to variable blanks for chloride and variable reactivity for NO_2 and SO_2 that can result in positive artifacts for nitrite and sulfate. The denuder difference method performed best of the methods tested, relative to an FTIR, for the

measurement of HNO_3 during the Nitrogen Methods Species Comparison Study (Hering et al.; 1988).

Hydrochloric Acid (HCl)

As mentioned in Section A.1.5, HCl concentrations in ambient air can be obtained continuously by TDLAS and by time-integrated measurements using filters and diffusion denuders. Collection of HCl by denuders can be done either by extracting the denuder coating and analyzing it directly for the concentration of the gas-phase species that have been collected on the denuder coating or by the denuder difference method (Solomon et al., 1988a, 1998b; Eldering et al., 1991). These are the same as the denuder methods for collecting HNO_3 and aerosol nitrate (Hering et al., 1988 and references cited therein; Solomon et al., 1988). In the first method, HCl is collected on a basic coating (e.g., Na_2CO_3 , KOH) applied to the denuder surface, extracted, and analyzed as chloride ion, e.g., by ion chromatography. As described above for HNO_3 and NH_3 and their aerosol counterparts, continuous methods using denuders coupled to ion chromatography are also capable of measuring HCl in near real-time.

In the second method, as described above for HNO_3 and NH_3 , the sampled air is split between a denuder-filter pack configuration (DF) and a filter pack (FP) only configuration. The filter in both configurations is a reactive filter that acts as a perfect sink for HCl (e.g., Na_2CO_3 , KOH, pre-washed nylon), not allowing particulate chloride to volatilize. The denuder is also coated with a basic material (e.g., Na_2CO_3 , KOH, MgO) that removes the acidic gases, including HCl. Gases are collected in the denuder and only particles are collected by the filter in the DF configuration. Both HCl and particulate chloride are collected on the filter in the FP configuration. The difference between the chloride ion measured on the two filters provides an estimate of gaseous HCl. The denuder difference method, using MgO coated denuders and KOH impregnated filters was used to examine the reaction of HNO_3 with sea salt particles (NaCl) producing HCl and coarse particle NaNO_3 in the Los Angeles air basin (Eldering et al., 1991). The denuder difference method also is suitable for measuring ammonia in air. In this case, the denuder and reactive backup filters are coated and impregnated,

respectively with citric acid. In fact, formate and aldehyde can be determined in this same manner using KOH as the reactive base (Solomon et al., 1998a); although PAN might interfere with the acetate measurement.

Continuous Methods:

Spectroscopic methods have been described earlier (see Section A.1.1). As described earlier for the measurement of sulfate and ammonium, HCl can be measured continuously using wet denuders coupled to an ion chromatograph.

A.2.4 Particle Number and Size Distribution

Physical properties of atmospheric particles, such as number concentration and size distribution, have been recently reviewed by McMurry (1998) for the 1998 NARSTO (North American Research Strategy for Tropospheric Ozone) Scientific Assessment of ozone-related science. A summary of some of the methods is given Table A-6. McMurry's critical review addresses methods for the measurement of particle physical properties and particle chemical composition. This section addresses only the measurement of physical properties of the particles, including total number concentration, cloud condensation nuclei concentration, and size-resolved measurements. In his review, McMurry provides a summary of measurement methods related to each property of the particle and discusses factors that affect measurement uncertainty for each individual measurement methods. Quantifying uncertainty with these measurements is problematic and depends on many assumptions, which are too lengthy to describe here. Therefore, we provide here only a brief summary of the methods and issues affecting their uncertainty and are providing only qualitative estimates of precision and accuracy in Table A-6. Readers are referred to McMurry (1998) for additional details.

Many of the instruments or methods indicated below have been used aboard aircraft and several have been intercompared aboard aircraft. However, problems result due to differences in sampling flow rates at the inlet and inlet transfer tubes versus the speed of the aircraft, which occurs even with isokinetic sampling inlets, due to

Table A-6. Measurements of Particulate Matter (Size Distribution and Related Particle Properties)

Method	Variable Measured	<u>Limit Detection</u>	<u>Precis ion</u>	Accuracy	Potential Interferences/Artifacts	References
Particle Counting/Sizing						
Optical Particle Counter/Sizer	Particle size via optical scattering amplitude	$< 1 \text{ particle cm}^{-3}$ $0.1 < d < 50 \text{ } \mu\text{m}$	Poor	Poor	Sensitive to particle shape, refractive index	Dick et al., 1994 Baumgardner, 1998
Aerodynamic Particle Sizer	Aerodynamic particle diameter				Sensitive to particle shape, density	Wilson and Liu, 1980
Condensation Nuclei Counter (CNC)	Density of nucleated particles	$< 1 \text{ particle cm}^{-3}$ $d > 0.01 \text{ } \mu\text{m}$	Excellent	Excellent	No size resolution Sensitive to small particles	Stolzenberg and McMurry, 1991
Differential Mobility Analyzer (DMA/CNDC)	Density of submicron particles	$< 1 \text{ particle cm}^{-3}$ $0.01 < d < 1 \text{ } \mu\text{m}$	Excellent	Good	Multiple charging for particles $> 0.1 \text{ } \mu\text{m}$	Wang, Flagan, 1990 Russel et al., 1996
Electrical Aerosol Analyzer	Density of submicron particles	$< ? \text{ particle cm}^{-3}$ $d > 0.01 \text{ } \mu\text{m}$	Good	Good	Multiple charging for particles $> 0.1 \text{ } \mu\text{m}$	Winklmayr et al., 1991

environmental changes during sampling, such as changes in temperature and pressure, and due to compression as gases and particles slow down in the sampling inlet (see Section A.8 for additional details regarding sampling aloft from aircraft platforms. Other uncertainties due to sampling aboard aircraft are summarized in McMurry (1998 and references cited therein).

Number Concentration

Particles, in the less than about $0.1\ \mu\text{m}$ size range (ultrafine particles) act as condensation nuclei for the formation of larger particles. The total number concentration of particles that act as condensation nuclei are determined by condensation nucleus counters (CNC). In this method, particles are grown by condensation of a liquid to the particle surface as particles pass through a supersaturated liquid, with growth factors of 100 to 1000. CNCs can detect individual particles as small as $0.003\ \mu\text{m}$ (3 nm); although this depends on instrument design and sampling pressure and for particles less than about $0.05\ \mu\text{m}$ on the size and composition of the particles (see McMurry, 1998 and references therein; Liu and Pui, 1974a). The upper size limit is about $0.5\ \mu\text{m}$ (Finlayson-Pitts and Pitts, 1986). The most common condensing vapors used in CNC are water and n-butyl alcohol. The original particle represents only a small fraction of the total particle after growth so factors such as particle shape and chemistry do not affect detection.

The CNC instruments in use today develops condensation to the particles based on steady-flow, forced-convection heat transfer. In this method, supersaturation is achieved by heat transfer from the warm aerosol ($35\text{-}40\ ^\circ\text{C}$) to the wall of the condenser ($\sim 10\ ^\circ\text{C}$) as the particles pass through a laminar flow condenser (Sinclair and Hoopes, 1975; Bricard et al., 1976). Two detection methods are employed in CNC counters: direct or single particle counting instruments and indirect detection instruments. Direct detection instruments determine particle concentrations by counting individual saturated particles. Uncertainties for single particle counting instruments are determined primarily by uncertainties in aerosol sampling rate, Poisson counting statistics, and minimum detectable size. Indirect measurement of particle number concentration is achieved by measuring light attenuation through or the light scattered by multiple droplets. These

instruments require calibration with an independent standard that can deliver known concentrations of particles. Currently, indirect-counting CNC instruments are calibrated using the differential mobility analyzer (DMA) that introduces into the CNC singly-charged, monodisperse particles selected from a polydisperse aerosol of known composition by electrostatic classification (Liu and Pui, 1974a). Uncertainties with indirect counting instruments depend on the accuracy of the calibration, instrument stability, signal-to-noise ratio, minimum detectable size, and sampling line losses. Typically accuracies of about 10% are obtained; although in the presence of high concentrations of nanoparticles larger uncertainties are observed (McMurry, 1998).

Cloud Condensation Nuclei Concentrations

Cloud condensation nuclei (CCN) counters measure the concentration of particles converted to cloud droplets by condensation of water at a specified supersaturation. This information is important for understanding chemical processing in cloud and fog droplets and the effect of clouds and fogs on the atmospheric radiation budget. Since saturation in clouds, occurs at water vapor supersaturations just over 100%, CCN counters operate at supersaturations of about 0.01 to 1% and only use water as the condensing liquid. Because of these lower saturation concentrations of the condensing fluid, the number of particles saturated and detected by the CCN is much lower than that with the CNC, which operates at several hundred percent supersaturation. Design parameters for CCN counters include the range of saturation ratios employed, the method used for determining the relationship between CCN concentrations and saturation ratio, and the particle growth time (e.g., 100 s for CCN at low supersaturations relative to the CNC counter that operates at 0.3 s) (McMurry, 1998).

A number of different approaches used in CCN instruments are described in McMurry (1998) and in a review of CCN instruments by Hudson (1993) and will not be repeated here. Differences in the methods relate to the design parameters mentioned above. The approaches summarized by McMurry include isothermal haze chambers (IHC), static thermal gradient diffusion cloud chambers, and continuous flow diffusion cloud chambers. Several instruments have been designed for use aboard aircraft and they

are summarized in McMurry (1998) as well. Three workshops have been held to compare the performance of various CCN counters. The three workshops were held in 1967, 1970, and 1980, the latter being the most comprehensive one (Journal de Recherches Atmospheriques, 1981, pages 181-373). Results from this third workshop indicate agreement among the same methods ranging from as good as 40% among the IHC methods to as good as 15 % among the other methods. Only the same methods can be compared as each method uses different design parameters and essentially measures difference size ranges of particles.

Size-Resolved Measurements

Several methods are available for measuring size distributions of particles in the atmosphere based on the different properties of the particles. These include sizing particles based on optical properties, aerodynamic size, electrical mobility, diffusion characteristics, and condensation relationships, the latter being discussed above with regards to number concentration. However, because these methods differ in the property of the particle they are measuring, different sizes can be reported for the same particle. For example, as summarized by McMurry (1998), the aerodynamic size obtained with impactors or other aerodynamic particle sizers depends on particle shape, density, and size, while electrostatic classification depends on particle shape and size, but not density, and optical sizes depend on particle refractive index, shape, and size. These sizes can be different from the geometric or Stokes sizes that would be observed in a microscope. However, converting from one measure of size to another can be done; although it may result in significant uncertainty (e.g., see Sloane, 1984; McMurry et al., 1996). For additional details on the methods described below, the reader is referred to McMurry (1998) and Finlayson-Pitts and Pitts (1986).

Impactors have been used to determine discrete size fractions of ambient aerosols, sized by aerodynamic diameter, in the size range from about 0.05 – 30 μm . Operating impactors at reduced pressures has extended the lower size range down to below 0.05 μm (Hering et al. 1978, 1979). Impactors operate by accelerating particles through an acceleration nozzle, which gives particles greater than a certain size sufficient momentum

to impact on a collection substrate, while smaller particles follow the air stream around the collector to either another, smaller acceleration nozzle-collection substrate pair or to a backup filter. The backup filter collects all particles less than the final collection surface. Several impactors are described by Finlayson-Pitts and Pitts (1986). Impactors have been designed with only one acceleration nozzle-collection substrate pair, while others may have up to 10 pairs, thus fractionating the aerosol into 10 size ranges. Real impactors employ a solid collection substrate (e.g., aluminum), while virtual impactors use a collection cone. Therefore, virtual impactors use still air as a virtual impaction surface. Particles penetrating the still air are collected in the collection cone passing through the still air barrier, while smaller particles flow around the cone and are collected separately from the larger particles. Virtual impactors do not suffer from particle bounce problems associated with real impactors; however, their cutpoint (i.e., the shape of the collection efficiency curve) is not as sharp as real impactors. For real impactors, the particle bounce can be minimized by conducting the measurements at a relative humidity in the range of 70 to 80% (Stein et al., 1994; Sorenson and McMurry, 1998; Vasiliou et al., 1998).

Light and electron microscopes can be used to determine particle sizes in the range from about 0.4 to 100 μm and about 0.001 μm or larger, respectively. These methods require collecting a small sample on a smooth flat surface and then counting and measuring the particles manually or by computer processing. This is a labor intensive method and is typically only used in conjunction with determining particle morphology or single particle chemical composition by scanning electron microscopy (SEM) where the electron beam causes the sample to emit fluorescent X-rays characteristic of the elements present in the sample. Thus, SEM allows for determination of chemical composition of individual particles.

Optical particle counters (OPC) measure the amount of light scattered by individual particles as they move across a focused beam of light. The scattered light is collected and converted into a proportional voltage pulse. Particle size is determined from the magnitude of this voltage using a calibration curve obtained using spherical particles of known size and composition. A review on the theory of optical aerosol behavior and its application to particle measurement is given in Willeke and Liu (1976). Gebhart (1993) reviews aerosol measurements by light scattering. OPC use either

incandescent (white) or monochromatic (lasers) light as their light source. White light OPC typically have minimum detection limits of about $0.3\ \mu\text{m}$, while laser OPC have minimum detection limits of about $0.05\ \mu\text{m}$ due to their higher illuminating intensity. Thus, laser OPC are more desirable for particles smaller than the wavelength of the illuminating light, while white light OPC are more advantageous for larger particles. In general, OPC measure particles in the size range from about $0.01\ \mu\text{m}$ to about $10\ \mu\text{m}$.

Determination of particle size from OPC response can be calculated from Mie theory and the refractive index of the measured particles. Uncertainties in the determination of size distributions result from not knowing the refractive index, shape, or morphology of the measured particles. To help reduce these uncertainties, Hering and McMurry (1991) calibrated the OPC with atmospheric aerosols of known size. They used an electrical classifier to determine particle size prior to delivering the particles to the OPC. Other particle properties (estimates of particle shape and/or refractive index) that can be derived from an OPC are summarized in McMurry (1998). Whitby and Willeke (1979) describe potential problems associated with optical particle counters and discuss ways to minimize the problems.

Aerodynamic particle size is inferred from particle velocity determined by the time-of-flight between two points separated by a known distance (Dahneke, 1973; Mazumder et al., 1991). At least three commercial instruments are available (Baron et al., 1993). The aerodynamic diameter is defined as the diameter of a unit density sphere that has the same settling velocity as the particle (Hinds, 1982), where settling velocity is the difference between aerodynamic drag and gravitational forces. The size range is from about $0.2\ \mu\text{m}$ (or $0.5\ \mu\text{m}$) to about $10\ \mu\text{m}$. The minimum size measured depends on the instrument design. This method can provide high-resolution aerodynamic size distributions in real time (McMurry, 1998).

Electric mobility analyzers classify particles according to electrical mobility, which depends on the number of elementary charges carried by the particle, the magnitude of the elementary unit of charge, a slip correction factor, the absolute gas viscosity, and the particle diameter, but does not depend on particle density. Currently, the differential mobility particle sizer (DMPS; Keady et al., 1983) is used to determine size distributions based on electrical mobility. DMPS includes a differential mobility

analyzer (DMA; Liu and Pui, 1974b; Knutson and Whitby, 1975) and a particle detector, typically a CNC.

In the DMA, particles receive a bipolar charge. Particles in a narrow mobility range are determined by the classifying voltage and flow rates. The complete size distribution is obtained by carrying out measurements at a number of classifying voltages. Size distributions typically require about 20 minutes to obtain; although shorter time frames are obtained by ramping the classifying voltage continuously. The voltage scanning approach is now typically used in determining atmospheric aerosol size distributions. Diffusion limits the lower size of particles that can be accurately measured using the DMPS to particles greater than $0.05 - 0.1 \mu\text{m}$; although recent work, summarized in McMurry (1998) describes approaches for determining particle sizes down to $0.003 \mu\text{m}$. Sizing particles at the high end of the size spectrum is limited to a maximum size of about $1 \mu\text{m}$. This limitation results because particles larger than about $1 \mu\text{m}$ in diameter contain a wide range of charges, and, therefore, apparent sizes. Multiple charges increase the difficulty of deconvoluting the data to determine the contribution of each size at a given classifying voltage. Measurement accuracies are affected by particle shape and are likely size dependent, but can not be determined at this time due to the lack of polydisperse aerosol standards (McMurry, 1998).

Diffusion of particles to a surface is a function of particle size with diffusivities increasing with decreasing particle size. Diffusion batteries are based on this size-dependent deposition rate. They are most commonly used for particles less than $0.1 \mu\text{m}$ in diameter, as diffusion coefficients are sufficiently high enough to result in significant deposition across the collection surface. The lower limit is around a few nm in diameter. The quality of data that can be obtained with diffusion batteries is limited due to the stochastic processes that govern diffusion. Thus, a wide range of particle sizes is deposited on each collecting surface, with the result that there is no simple relationship between the change in aerosol concentration collected across the collecting surface and particle size. Therefore, in recent years diffusional separation has been replaced by electrostatic classification as described above.

A.2.5 Water Associated With Particles

The measurement of water associated with particles is problematic, as it must be done without disturbing the particle/gas-phase water equilibrium. Several methods have been used, including microwave resonance (Ho et al., 1974), gravimetric analysis at varying relative humidities (Hänel and Lehmann, 1981), beta-gauge measurements of mass at varying relative humidities (Speer et al., 1997), and measuring particle mobility at two different relative humidities using the tandem differential mobility analyzer (TDMA) (Rader and McMurry, 1986; Saxena et al., 1995; McMurry, 1998). The TDMA measures water associated with particles in the 0.02 – 0.5 μm size range; although work is underway to expand this range to particles of 1 μm in diameter by using an aerosol concentrator (McMurry, University of Minnesota, personal communication, 1998). Other possible but less accurate methods for estimating water associated with particles involves measuring the difference in scattering properties of particles at two temperatures using two nephelometers, one at ambient temperature and one heated (Richards, STI, personal communication, 1998), and measuring the difference in mass on two TEOMs at two different sampling temperatures. The advantage of these last two methods, if they can be shown to provide suitable estimates of water associated with particles, is that they are much less expensive and are easy to use.

None of these methods provides direct measurements of water content as all methods involve taking the difference between two parameters (e.g., mass, scattering, mobility) and do not detect hydrated water; rather they detect condensed water that is in equilibrium with the gas-phase, based on varying relative humidity or varying temperature. An independent method relies on the use of thermodynamic models to calculate water content (e.g., Pilinis et al., 1989). However, these models only include water associated with ionic species (e.g., sulfate, nitrate, and chloride) and do not include water associated with organic material, which has been shown to be important (Saxena et al., 1995; Saxena and Hildemann, 1996). Since water can contribute significantly to aerosol mass, (e.g., 50% of the fine particle mass at relative humidities exceeding 70%; Hänel, 1976; Zhang et al., 1993), it is important that methods to measure water associated with particles be developed.

A.3 Measurements in fogs and clouds

Fog and cloud collectors are designed to collect water droplets in the size range from 2 to 50 μm , as opposed to the collection of atmospheric particles that typically are sampled in the less than 10 μm or less than 2.5 μm size ranges. Collectors that collect all droplet size ranges are referred to as bulk collectors, while others collect two or more independent size fractions. Fog and cloud droplet collectors, typically collect the water droplets by impaction on a surface, either actively or passively. If the collection surface is moving or if air and droplets are being drawn across the collection surface, then the sampler is referred to as an active sampler. Passive samplers rely on air movement due to atmospheric flow to move the droplets across the collection surface. Pandis et al. (1995) recently reviewed fog and cloud droplet samplers. Table A-7 presents a summary of measurement techniques for fog chemistry.

A.3.1 Bulk fog/cloud water detectors

These fog samplers collect all drop sizes in a single fraction. Passive samplers consist of a collection surface and a plate or a series of strings or rods. Fog impacts the collection surface and is collected by gravity in a container for additional analysis in the laboratory. The design of the collection surface and the speed of the wind define the size range of droplets collected. These collectors are used in areas where power is difficult to obtain.

Active samplers developed since the early 1980s are summarized in Pandis et al. (1995), while ones developed prior to the early 1980s are summarized in Jacob et al. (1984). The most recent methods for collecting fog droplets use a fan to pull air across Teflon stands (Demoz et al., 1996). Teflon strands are used in the Caltech Active Strand Cloudwater Collector (CASCC; Daube et al., 1987; Demoz et al., 1996) and in a later version of the CASCC (CASCC2; Collett et al., 1994; Demoz et al. 1996; Rao and Collett, 1995). The CASCC series of fog collectors have been widely used in fog experiments in the United States (see Pandis et al., 1995). The CASCC and the CASCC2

Table A-7. Measurement of Fog Chemistry

Method	Variable	Limit of Detection (μN)	Precision ¹ (relative standard deviation %)	Accuracy	Comments	References
pH electrode	H ⁺ (as pH from 2.9 – 7)		(0.05 pH units)			Collett et al. (1994)
Ion Chromato-graphy	Cl ⁻	1.4	5.1	8%		Collett et al. (1997)
	NO ₃ ⁻	0.8	0.3	7%		Collett et al. (1997)
	SO ₄ ⁻	1.3	1.1	Better than 5%		Collett et al. (1997)
	Na ⁺	0.9	1.2	Better than 5%		Collett et al. (1997)
	NH ₄ ⁺	1.2	0.6	Better than 5%		Collett et al. (1997)
	K ⁺	1.0	3.1	Better than 5%		Collett et al. (1997)
	Mg ⁺²	0.8	5.3	Better than 5%		Collett et al. (1997)
	Ca ⁺²	0.9	4.2	Better than 5%		Collett et al. (1997)
	Acetate	1.1	2.6			Collett et al. (1997)
	Propionate	2.0	7.9			Collett et al. (1997)
	Formate	2.0	0.7			Collett et al. (1997)
	Pyruvate	0.8	0.2			Collett et al. (1997)
	Oxalate	5.45	0.7			Collett et al. (1997)
Colorimetric	S(IV)	0.9	14.4		Sample preserved in the field	Collett et al. (1997)
	HMS	0.9	14.4		Sample preserved in the field	Collett et al. (1997)

¹ Samples collected using a variety of fog collectors. Precision represents analytical uncertainty based on replicate measurements of the same sample. Overall uncertainty would be slight higher due to uncertainty in sampling flow rates. In percent unless noted otherwise.

Table A-7. Measurement of Fog Chemistry (continued)

Method	Variable	Limit of Detection (μN)	Precision ¹ (relative standard deviation %)	Accuracy	Comments	References
Fluorescence	Formaldehyde	0.2	5.3		Sample preserved in the field	Collett et al. (1997)
Fluorescence	H ₂ O ₂ /Organic Peroxides	0.5	5.6		Sample preserved in the field	Collett et al. (1997)
Total organic carbon analyzer	TOC	1.3	10.8		OC converted to CO ₂	Collett et al. (1997)
	TDOC	1.3	10.8		OC converted to CO ₂	Collett et al. (1997)
Graphite Furnace Atomic Absorption	Iron	1.8	5.0		With Zeeman correction	Collett et al. (1997)
	Manganese	0.2	8.6		With Zeeman correction	Collett et al. (1997)

both have 50% collection efficiencies or droplet size cutpoints at about $3.5\ \mu\text{m}$. The CASC is a larger instrument operating at about $24.5\ \text{m}^3\ \text{min}^{-1}$, while the CASC2 is considerably smaller and operates at $5.8\ \text{m}^3\ \text{min}^{-1}$. Fog or cloud droplets can be collected with a time resolution of about 5 to 10 minutes using the CASC and about 20-30 min using the CASC2. Comparison of liquid water content obtained from the CASC, CASC2 and an independent technique, the Gerber Particle Volume Monitor showed good agreement (PVM-100) (Gerber, 1989; 1991). Fog or cloud water samples collected using these samplers can be analyzed for chemical species, as described below, and for liquid water content as described in Demoz et al. (1996).

A.3.2 Size-Selective Collectors

Several instruments have been designed to collect fog and cloud droplets in two or three size fractions (Noone et al., 1988; Munger et al., 1989; Schell and Georgii, 1989; Hindman et al., 1992; and Collett et al., 1993, 1995). These samplers either use multiple rows of strands in series, where each row consists of a different size strand, and therefore, collects different size droplets, or they consist of impaction plates similar to particle impactors with different size acceleration nozzles in each plate. As an example, the size fractionating CASC (sf-CASC) operates at $19\ \text{m}^3\ \text{min}^{-1}$, uses two rows of Teflon stands in series, and collects fog in two size ranges, greater than $23\ \mu\text{m}$ and between 4 and $23\ \mu\text{m}$ in diameter (Munger et al., 1989a; Demoz et al., 1996). As with the other strand collectors, drops impacting on the stands drain into collection vials below the sampler. This sampler, as with its bulk counterpart can collect tens to hundreds of ml per hour of liquid water (depending on the water content of the fog or cloud) and provides sufficient sample for chemical analysis of the collected fog or cloud water. However, the cutpoint efficiency is not as sharp as those described below that use impaction plates, similar to particle impactors. Other size-selective strand collectors are described in Pandis et al. (1995).

Collett et al. (1993) describe a two-stage cloud impactor that provides lower size-cuts (50 % collection efficiency) of 3 and $10\ \mu\text{m}$ diameter at a flow rate of $418\ \text{l}\ \text{min}^{-1}$. Thus, two size fractions are obtained, one above $10\ \mu\text{m}$ and one between 3 and $10\ \mu\text{m}$ in

diameter. Because the fog water sample is split into two fractions, sampling times on the order of 30-60 min are required to collect sufficient sample for chemical analysis. A three-stage impactor, larger than the two-stage impactor is described by Iovinelli (1994) and Collett et al. (1995). This collector operates at 1500 l min^{-1} . The three-stage and a modified two-stage collector were designed with interchangeable impaction plates allowing for the collection of different size ranges with lower size cuts of 3, 5, 10, 14, and $21 \text{ }\mu\text{m}$ droplet diameter for the two-stage collector and 3, 4, 10, 12, 15, 20, and $30 \text{ }\mu\text{m}$ for the three-stage collector. Only two or three size ranges are collected, respectively, during a given sampling period (Pandis et al., 1995). Recently a five-stage cloud impactor has been developed (Collett et al., 1998) which simultaneously collects droplets with lower size cuts of 4, 10, 15, 25, and $30 \text{ }\mu\text{m}$ droplet diameter. This latter sampler has been designed, not only to collect additional simultaneous size fractions, but operates at a higher volume ($2,000 \text{ l min}^{-1}$ versus about 500 l min^{-1}) is more compact, and uses a single rectangular acceleration jet rather than a series of circular jets. The smaller size of the collection area also helps to minimize contamination.

A.3.3 Liquid water content of fogs and clouds

Several intercomparisons for estimating liquid water content by various methods have been conducted (Arends et al., 1992; Berner, 1988; Baumgardner, 1983; Demoz et al., 1995). Methods included in the various comparisons, although not all at the same time, were the Gerber Particle Volume Monitor, the Forward Scattering Spectrometer Probe (FSSP-100); and estimates from fog collectors. A summary of these intercomparisons is given in Pandis et al. (1995). The Gerber Particle Volume Monitor estimates liquid water content by measuring light scattered in the near forward direction by fog or cloud droplets passing between a laser source and a detector (PVM-100; Gerber 1989; 1991). This instrument is becoming popular for measuring liquid water content in fogs and clouds. Estimates of liquid water content from fog collectors are also becoming more popular, but they are complicated due to the need to correct for the collection efficiencies for each collected size fraction. Demoz et al. (1996) describe the calculations and uncertainties for the active strand series of cloud/fog water collectors. Agreement

among the different methods observed during these intercomparisons for the estimation of liquid water content in fogs and clouds was typically within 10%, with the exception of the FSSP-100 and the PVM-100, where the FSSP-100 estimated values 20-30% higher than the PVM-100 (Arends et al., 1992). Using gravimetric filter sampling as the reference for the study, Arend et al. (1992) determined that the best performance was obtained with the PVM-100.

A.3.4 Chemical composition of fog and cloud droplets

Several inorganic and organic anions and cations are typically determined in fogs to elucidate the chemical behavior and dynamics within fogs and clouds (see for example, Collett et al., 1997; Collett et al., 1998a; Collett et al., 1998b; Jacob et al., 1989; Munger et al., 1983; Collett et al., 1989). Important species analyzed include inorganic anions (Cl^- , NO_3^- , and SO_4^{2-}), inorganic cations (H^+ [as pH], Na^+ , K^+ , NH_4^+ , Ca^{2+} , and Mg^{2+}), total Fe and Mn, low molecular weight organic anions (formate, acetate, propionate and pyruvate and others), formaldehyde, S(IV), hydroxymethylsulfonic acid (HMSA), hydrogen peroxide, and organic peroxides. Successful determination of some of these species requires stabilization in the field immediately after sample collection. In general, the analytical methods for determining the concentration of these species in fogs and clouds are now well established and will only be summarized here. Analytical limits of detection and analytical uncertainties are given in Collett et al. (1997) based on results from the 1995 Integrated Monitoring Study (IMS95; Solomon et al., 1996). The reader is referred to Pandis et al. (1995) and Collett et al. (1997) for additional details.

In the methods described below, sample concentrations are determined against calibration curves of response against known concentrations, with corrections for blanks and interferences where known. Ambient concentrations are determined by knowing the total volume of water collected and air volume sampled. Precision is typically determined by analysis of split samples; although in a few cases it was determined by analysis of replicate standards. Examples of quality control, quality assurance, and data validation procedures are summarized in Collet et al. (1997). Detailed descriptions of how uncertainties and detection limits can be calculated for fog sampling is also given in

Collett et al. (1997) along with calculated values determined based on the experience with IMS95, and intercomparison results.

pH

Collected fog or cloud water pH is determined immediately after sample collection with a combination electrode pH meter. The hydrogen ion concentration can then be determined from pH by standard methods. Precision has been determined for pH measurements in fog samples by making 10 replicate pH measurements each from separate aliquots of 18 different fog and cloud samples with pH values ranging from 2.9 – 7.0. Standard deviations from the 10 replicate measurements ranged from 0.01 to 0.11 pH units. The standard deviation tended to increase as sample pH increased. Only two of the eighteen samples had standard deviations greater than 0.05 pH units. Both had mean pH values greater than 6.2 (Collett et al., 1994).

Inorganic anions and cations (Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , NH_4^+ , Ca^{2+} , and Mg^{+2})

These species are most often determined by ion chromatography. Example analysis conditions are given by Collett et al. (1997). Metal cations can also be determined by atomic absorption spectroscopy and ammonium ion (NH_4^+) by automated colorimetric analysis. Limits of detection by these methods are similar.

Organic acids

These species are most often determined by ion chromatography. Example analysis conditions are given by Collett et al. (1997).

Total S(IV) and hydroxymethanesulfonic acid (HMSA)

Free S(IV) in cloud or fog water can be easily oxidized by dissolved oxidants (H_2O_2 , O_3 , and O_2) in the presence of transition metals. Therefore, samples are preserved

immediately after collection by adding a preserving solution containing formaldehyde, sodium hydroxide, and CDTA (trans-1,2-cyclohexylenedinitrilo-tetraacetic acid). Addition of the preserving solution allows free S(IV) to be complexed with formaldehyde to form hydroxymethane sulfonic acid (HMSA), which is not easily oxidized. The HMSA is decomposed to free S(IV) before analysis. The CDTA is added to prevent interferences from trace metal and a catalase solution is added to destroy any H₂O₂ in the collected sample, since oxidation of S(IV) by H₂O₂ is fast and could interfere with the measurement.

HMSA originally present in the fog or cloudwater sample is preserved as described above for S(IV), however, excess H₂O₂ is first added to remove free S(IV) present in the sample. Free S(IV) is then determined by difference.

The analysis of S(IV) complexed as HMSA plus HMSA, and HMSA by itself is performed as follows. First, HMSA is decomposed to formaldehyde and S(IV) by a strong base followed by reaction of S(IV) and formaldehyde with acidic pararosaniline to form a purple compound that is measured spectroscopically.

Formaldehyde (CH₂O)

Formaldehyde needs to be preserved in the fog or cloudwater samples immediately after collection. This is done by adding bisulfite to form HMSA. In the laboratory, HMSA is decomposed to formaldehyde for analysis by fluorescence. Formaldehyde reacts quantitatively with 2,4-pentanedione and ammonia to form a yellow product, diacetyldihydrolutidine (DDL). The concentration of DDL is then determined by fluorescence spectroscopy.

Hydroperoxides

Hydrogen peroxide and soluble organic hydroperoxides need to be preserved immediately after sample collection. This is done by adding *p*-hydroxyphenylacetic acid (POPHA) and peroxidase to form a stable dimer, and a conditioning reagent. The conditioning reagent contains potassium hydrogen phthalate (KHP), which acts as a

buffer (pH = 5.5), and EDTA that prevents interference by metal ions and also acts a buffer in the same pH range. The hydroperoxides are then determined as the dimer by fluorescence spectroscopy, since there is a 1:1 correspondence between the dimer and hydroperoxides.

Total Fe and Mn

To stabilize these species in the field, fog and cloud samples are acidified with nitric acid immediately after collection. Concentrations are determined by either atomic absorption spectroscopy or graphite furnace atomic absorption spectroscopy (GFAAS). Collett et al. (1997) employ Zeeman corrected GFAAS.

Total organic carbon (TOC) and dissolved organic carbon (DOC)

In the field after sample collection, fog or cloudwater is split into two fractions. The first fraction is added directly to a clean glass vial that provides a sample for the determination of total carbon and total inorganic carbon. The difference represents an estimate of total organic carbon. The second fraction is filtered before adding it to a second clean glass vial. This sample is analyzed for dissolved carbon and dissolved inorganic carbon with the difference representing an estimate of dissolved organic carbon. The collected samples are analyzed using a total organic carbon analyzer. Total carbon content is obtained by vaporization and decomposition of the sample at 680 °C, with measurement of evolved CO₂. Inorganic carbon is determined by reacting the sample with 25% phosphoric acid followed by the measurement of evolved CO₂. Elemental carbon is not measured by this method since the furnace temperature is too low to oxidize it to CO₂.

A.4 Meteorological measurements

A.4.1 Temperature

Accurate measurements of temperature at ground-level and aloft are essential for understanding the kinetics of atmospheric processes and for determining boundary layer characteristics (e.g., the height of the boundary layer and its structure). Ground-level methods are routine, precise, accurate, and inexpensive. Measurements aloft are somewhat more expensive and typically less accurate since calibration methods are difficult. Table A-8 presents a summary of measurement methods for atmospheric temperature.

Measurements at the Surface

Most *in situ* temperature measurements use the fact that many electrical properties are a known function of temperature. Instruments are based on resistance variation (thermistors), capacitance or thermocouple. The time constant for adjustment to a new temperature is a few seconds and the accuracy is better than 1°C. The sensor must be placed in a ventilated housing to shield it from direct solar radiation. The best instruments are ventilated by a fan, rather than relying on the wind.

Measurements Aloft

The instruments used to measure temperature at the surface can be installed on an airborne platform (e.g., aircraft or radiosonde) to obtain data aloft. For measurements conducted with a radiosonde (see Section A.4.3 for a brief description of the tracking system), the vertical resolution of the measurement is in the range of 5 to 10 m. The signal typically can be tracked up to about five kilometers of altitude, depending on the meteorological conditions. However, the temperature data obtained by radiosondes vary in both space and time as the balloons are carried by the wind, and the amount of information is rapidly limited by the costs associated with the instrument platform.

Table A-8. Measurements of temperature

Method	Variable Measured	Range	Resolution	Accuracy	Potential Interferences/ Artifacts	Comments	References
Thermistor	Temperature	-40 to + 70°C	0.1°C	0.1°C (>0°C) 0.2°C (<0°C)		Needs ventilated housing	Sutron
Platinum resistance	Temperature	-30 to +70°C	0.1°C	0.3°C			Handar
Capacitive bead	Temperature	-90 to + 60°C	0.1°C	0.2°C	Accuracy degrades at high altitude	Radiosondes, upper air	Vaisala
Satellite sounding	Temperature profiles	Complete range of possible temperatures		~1°K	Influence of first guess	Low vertical resolution. Global coverage	J. Clim. Appl. Meteor., 24, 128-143, 1985
RASS	Virtual temperature	Normal range of temperatures		0.5°K	Accuracy varies according to meteorological conditions	Measured volume: a few hundred meters	Remtech

Remote sensing techniques can be used to measure temperature aloft; then, the temperature data are recorded continuously as a function of height above a fixed ground location.

Since everything emits infrared radiation which depends on temperature, one can in principle measure temperature remotely by measuring the emitted radiation. That is the principle of satellite temperature profiler. The radiation emitted by the carbon dioxide of the atmosphere is measured at several wavelengths that have different emissivity and absorptivity. Since the carbon dioxide mixing ratio is approximately constant, the emission depends mainly on temperature. Simply stated, one can say that the radiation received by the satellite at each wavelength has been emitted by a different layer of the atmosphere. If the absorptivity at that wavelength is high, the emitting layer is at high altitude since radiation emitted by the lower layers is absorbed before reaching the satellite. Conversely, low absorptivity wavelengths come mainly from the lower layer where the density and temperature are high.

The early methods to convert the radiation measurements to temperature profiles were based on statistical regression. They were fast and robust, but not very accurate. Current methods make use of the radiative transfer equation. As mentioned above, these methods require the use of a first guess of the temperature profile, which introduces some uncertainty in the estimation of accuracy.

Another remote sensing technique is the ground based radio-acoustic sounding system (RASS). It operates in conjunction with a radar wind profiler. Pulses of microwaves and acoustic waves are sent vertically. Virtual temperatures are recovered by measuring the electromagnetic energy scattered from the acoustic wavefront (Virtual temperature is the temperature that dry air would have if it had the same density as the actual moist air at the same pressure. The RASS actually measures the air density and the temperature is derived from the perfect gas law. However, since the humidity is not known, one uses the gas constant for dry air and one obtains the virtual temperature). The propagation speed of the acoustic wave is proportional to the square root of the virtual temperature. Coincident measurements of humidity are needed to recover temperature. The vertical resolution obtained with a RASS is typically of the order of 50 - 100 m. The

maximum vertical range is typically of the order of a couple of kilometers, and the lowest level of measurement is typically centered at about 100m.

A.4.2 Humidity

Measurements of humidity are essential for understanding the chemical characteristics and chemical equilibrium between the gas and particulate phases of atmospheric aerosols. Ground-level measurements are routine, accurate, and inexpensive, except at high relative humidities above about 95 – 98% depending on the sensor. Measurements aloft are somewhat more expensive and typically less accurate since calibration methods are difficult. Table A-9 presents a summary of methods available to measure relative humidity.

Measurements at the Surface

There are many methods of measuring humidity. One is to measure the change of capacitance of a thin film with moisture. Other sensors use the change in electrical resistance of a thin film with humidity.

Wet and dry bulb sensors measure the differential temperatures of two standard electronic temperature sensors in ambient conditions. One sensor has its probe covered by a wick which remains in a moistened condition by absorbing water from a reservoir. This "wet bulb" sensor has a lower temperature reading owing to the cooling effect of evaporation of moisture from the wick. One can then calculate the ambient relative humidity by comparison between the dry and wet bulb temperatures.

Dewpoint sensors are based on the fact that moisture condenses as dew on a cooled surface. Typically, a chilled mirror is used. Condensation on the mirror drastically changes its reflectivity, thus making it possible to measure the dewpoint accurately.

Table A-9. Measurements of humidity

Method	Variable Measured	<u>Range</u>	Resolution	Accuracy	Potential Interferences/ Artifacts	Comments	References
Wet & dry bulb thermometers	RH computed from wet bulb temperature	0 to 100% RH		2% RH			Monitor Sensors
Chilled mirror	Dewpoint	-50 to + 100°C		0.2°C	Mirror could become contaminated with dust	Accuracy translates to about 5% in RH. More accurate at low humidity	EdgeTech
Thin film capacitor	Relative humidity	0 to 100% RH	1% RH	2 to 5% RH	About 1s lag. Possible wetting in clouds	Radiosondes, upper air	Vaisala
Raman lidar	Mixing ratio			.05 g/kg (night) 1 g/kg (day)	Background radiation interference during the day		Appl. Optics, 31, 3068-3082, 1992.

Measurements Aloft

As for temperature, the measurement techniques used to obtain an estimate of relative humidity near the surface, can be installed on an airborne platform (e.g., aircraft or radiosonde) to obtain information on relative humidity aloft. For example, cooled mirrors are used in some airplanes. Typically, instruments based on a thin film capacitor or a carbon hygistor are used in radiosondes, because such instruments can be made very light. The spatial resolution and vertical range for relative humidity measurements are the same as for temperature. However, the same limitations as those mentioned for temperature apply; i.e., the measurements are limited in space/time and the cost rapidly becomes prohibitive. There are several remote sensing techniques that can be used to measure relative humidity as a function of height above a fixed ground location.

A promising experimental method of measuring moisture in the vertical direction is the Raman lidar developed by Sandia National Laboratories (NOAA in Boulder, CO). The Raman effect principle is that water vapor molecules that are excited by a beam of light at a certain frequency re-emit radiation at a different frequency. The return signal is proportional to the water vapor concentration. Comparisons with radiosondes during the Atmospheric Radiation Measurement program of DOE indicate that these measurements have high accuracy.

A.4.3 Wind Speed and Direction

Measurements of wind speed and wind direction (WS/WD) are critical to understanding transport and mixing of pollutants within and above the boundary layer. Measurements at the surface are routine, precise, accurate, and inexpensive. Measurements aloft that are accurate are now obtained fairly routinely on a continuous basis. Compared to intermittent methods, they are not necessarily more expensive, given the wealth of added information obtained. Table A-10 summarizes measurement methods to characterize wind speed and direction.

Table A-10. Measurements of wind

Method	Variable Measured	Range	Resolution	Accuracy	Potential Interferences/Artifacts	Comments	References
Cup anemometer	Wind speed	0.5 to 50 m/s	0.1 m/s	2.5%	Can be affected by icing	Several models available with slightly different specifications	Monitor Sensors
Wind vane	Wind direction	0 to 360 deg	3 deg	5 deg	Can be affected by icing	Wind speed needs to be >0.2 m/s	Monitor Sensors
Ultrasonic	Wind components	0 to 65 m/s	Speed: 0.05 m/s Direction: 1deg	0.135 m/s 2 deg			Handar
Rawinsonde	Wind speed, direction	No limit	0.5 m/s 10 deg	.5 m/s 10 deg	Accuracy degrades at high altitude	Direction is truncated to tens of deg in the reports	Vaisala
Wind profiler	Wind components			0.75 m/s	Possible ground clutter	Profiles from 100m to 5000m in 50 – 100 m increments	J. Atmos. and Oceanic Tech. 12, 421-426, 1995
Doppler sodar	Wind components	0 to 45 m/s		0.25 m/s 2 deg		50 – 1500 m; 30 – 50 m for minisodars	AeroVironment
Doppler radar	Radial wind velocity	0 to 80 m/s		~2 m/s	Possible ground clutter. Aliasing of wind speed greater than range maximum	Signal strength depends on aerosol amount	Doviak and Zrnica, 1984

Measurements at the Surface

The traditional method of measuring wind at the surface is with a three-cup anemometer, combined with a wind vane. The speed of rotation of the anemometer is proportional to the wind speed. Because of inertia, the anemometer cannot measure near calm winds (< 0.5 m/s) reliably, although lower wind speed thresholds, down to about 0.2 m/s can be obtained with precision and well maintained standard anemometers. Without special precautions, cup anemometers may also be sensitive to icing.

Hot wire anemometers detect the wind speed through minute temperature differences between wires placed in the wind and in the wind shade (the lee side).

Another method uses ultrasound to determine horizontal wind speed and direction (sonic anemometer). The measurement principle is based on transit time, the time it takes for the ultrasound to travel from one transducer to another, depending on the wind speed along the ultrasonic path. The transit time is measured in both directions. For zero wind speeds, the forward and reverse transit times are equal. With wind along the sound path, the upwind transit time increases and the down wind transit time decreases. Using these two transit time measurements, the instrument computes the wind speed along the path. The accuracy of the computed wind speed is independent of altitude, temperature and humidity. The method described for one path is repeated to determine the wind speed along each of three paths that are offset by 120 degrees with respect to each other. The micro-controller computes the wind speed and direction, as well as the rectangular components.

For calm conditions with wind speeds less than 1 m/s, and certainly less than 0.5 m/s, the use of sonic anemometers is recommended since these instruments can detect wind speeds as low as 0.05 m/s whereas standard cup anemometers typically have higher thresholds as mentioned above.

Measurements Aloft

In the free atmosphere, the traditional way of measuring the wind is by following a radiosonde as it ascends (also called rawinsonde or pilot balloon). A radio theodolite

measures the azimuth and elevation angles of the balloon relative to the ground station as the balloon rises. The tracking is done automatically using the radiosonde transmitter signal (some systems use optical tracking, which is not as reliable as radio tracking). Upper air winds are then calculated by the computer from the theodolite data. The spatial resolution for wind measurements is typically of the order of 50 m (i.e., coarser than for temperature and relative humidity measurements) with a vertical range of several kilometers (typically 3 to 5 km, but possibly up to 10 km). However, these measurements provide data at specific times only, and temporal resolution is limited by the number of rawinsondes released.

For continuous measurements, several techniques exist. For example, radar wind profilers are now used in many field measurement programs. A wind profiler operates by transmitting electromagnetic energy into the atmosphere and measuring the strength and frequency of backscattered energy. The Doppler shift of the returned signal gives a measure of the air motion. By making measurements in several directions and averaging over a few minutes to eliminate the effect of turbulence, the total wind vector can be measured. The vertical range of a radar profiler is typically of the order of 5 km with a resolution of about 50-100 m.

The wind profile can also be measured with a Doppler sodar, which is based on the same principle as the radar wind profiler, but uses sound waves instead of electromagnetic waves. The altitude range sampled by a sodar varies according to the frequency used in the instrument, but also according to the environmental conditions (e.g., atmospheric turbulence, background noise). A “mini-sodar” with a frequency of about 4 KHz will typically have a vertical range from about 15 m to a few hundred meters. A “mega-sodar” with a frequency of less than 1 KHz can have a range of up to a few kilometers. The spatial resolution varies from about 10 m for a mini-sodar to about 100 m for a mega-sodar. Comparison of sodar measurements with tower-based measurements showed good agreement with a correlation of 0.92 (Crescenti, 1997).

Doppler radars work on the same principle as wind profilers, but instead of a fixed, phased array antenna pointing vertically, the antenna is a rotating dish. The wind speed in the direction of the beam can be mapped over several hundred km². By processing the signal, the complete horizontal wind field can be retrieved. Doppler

radars can only measure radial winds within a certain range (the Nyquist interval); if the actual winds are outside that range, they will be aliased, that is they will appear to "wraparound" to the opposite value. The reason for this aliasing is the fact that the radar pulse has a finite length. When a Fourier transform is applied to the return signal to get its frequency spectrum, only a limited band of frequencies can be obtained. Any frequency shift larger than a certain limit (corresponding to strong wind) will be aliased to a different value of the opposite sign. By using special processing of the results, which assumes continuity of the wind speed, some of this aliasing can be eliminated.

A.4.4 Mixing Height

The mixing height can be deduced from vertical temperature profiles. In addition, some sodars and radar profilers can provide information on the mixing height (Lindsey et al., 1996). These instruments use the fact that the radar reflectivity is related to the refractive index structure parameter and that this parameter peaks at the top of the convective mixing layer (i.e., bottom of the inversion layer). Typically, low level inversions (e.g., less than 300 m above ground level) cannot be resolved using this technique.

A.4.5 Solar Radiation

Pyranometers and radiometers that measure the solar radiation are based on the photo-voltaic principle. Various shading geometries make it possible to measure the direct solar radiation or the indirect radiation scattered by the whole sky. Some instruments measure total solar radiation whereas others measure U.V. radiation. Table A-11 summarizes the typical characteristics of photo-voltaic instruments.

A.4.6 Fog and Clouds

A discussion of techniques to measure the liquid water content of fog was provided in Section 3.4. The spatial coverage of fog can be determined via human

Table A-11. Measurements of solar radiation

Method	Variable Measured	Range	<u>Resol</u> <u>ution</u>	Accuracy	Potential Interferences/ Artifacts	References
Pyranometer (silicon photovoltaic)	Total solar radiation	Whole range of daylight conditions	2 Wm ⁻²	3 to 5%	Slight temperature dependence	Sutron

observations, measurements or satellite data. First, an operational definition of fog is needed to characterize the spatial extent of the fog. Standard procedures from the National Weather Service define fog to be present when atmospheric visibility (visual range) is 6 miles or less and relative humidity is 86% or more (dew point depression of 4°F or less). Visibility less than 6 miles with relative humidity less than 86% is defined as haze. These definitions are arbitrary and are, therefore, subject to uncertainties. Automatic visibility sensors can be used in conjunction with measurements of relative humidity to record the presence of fog. Satellite data that provide enhanced fog imagery may be very useful for areas where the areal coverage of the fog is significant.

The presence of clouds can be determined via human observations, airborne measurements, and satellite data. Trained human observers will report estimated height and type of clouds, following National Weather Service procedures. However, human observations are generally limited in their spatial coverage. Aircraft have been used to sample in clouds and can, therefore, characterize the liquid water content. Satellite imagery is particularly useful to characterize cloud coverage over large regional domains.

Ceilometers are lidars that measure the height of clouds. For example, Vaisala makes one that can detect 3 cloud layers simultaneously, up to 7.5 km in height. Vertical resolution is 50 ft with an accuracy of 25 ft. It uses special transmitting and receiving optics so that beam overlap is almost eliminated and detection of thin clouds as low as about 15-50 m above the ceilometer is possible.

A.5 Emission Inventories

An emission inventory plays a vital role in various aspects of current air quality management practices. Emission inventories are used to assess contributions of individual sources or group of sources in a region, as input data for source-oriented air quality models, and in the development and implementation of control strategies. The requirements (in terms of their spatial and temporal resolution) for emission inventories in modeling applications are significantly more demanding than for assessment studies. For example, emission inventories used for PM and visibility modeling need to be spatially and temporally resolved in a manner that is consistent with the model

formulation. Emission data for PM and visibility modeling need to be chemically resolved too, in order to adequately track the complex chemistry that occurs throughout a region of interest. A discussion of emission inventories can be based either on the type of sources of emissions (e.g., stationary, mobile) or on the emitted chemicals (e.g., SO₂, NO_x, VOC). Our discussion of emission inventory development uses the latter approach (Section A.5.1) but our discussion of testing emission inventory with field measurements is more conducive to using the former approach. A standard approach to estimate emissions of a pollutant is to use the following mathematical relationship:

$$E = \sum_i EF_i \cdot O_i \cdot (1 - h_i) \quad (\text{A-1})$$

where EF = Emission factor for the production of the pollutant by source i, e.g., amount of SO₂ emitted per ton of coal burned, amount of NO_x per vehicle mile traveled

O = Operating rate or activity level of source i, e.g., tons of coal combusted by power plants, the distance traveled by motor vehicles

η = Efficiency of the control device used by source i

Emission factors are given in compilations (e.g., AP-42) or are calculated by emissions models (e.g., PART5 for motor vehicles, BEIS for biogenic hydrocarbon emissions). Uncertainties in emission estimates are due to uncertainties in each of the three terms on the right hand side of Equation (A-1). A discussion of uncertainties in estimating emissions using an emission factor-based approach is provided in Pai et al. (1998b). Additional uncertainties can arise due to exclusion of sources and the inability of annual average emissions (typically calculated using Equation A-1) to capture the temporal variability, e.g., seasonal or weekday versus weekend.

In Section A.5.1, we discuss the current emission estimation techniques and their limitations in estimating emissions from major source categories of atmospheric PM and the chemical precursors of secondary PM. In Section A.5.2, we review measurement

techniques that can be used to validate emission inventories for PM and visibility modeling.

A.5.1 Current estimation techniques and their limitations

Particulate Matter (PM)

The dominant sources of primary PM in the United States include fugitive sources of dust from unpaved roads, paved roads, farming operations, construction activities and wind erosion. Emission rates for fugitive dust are difficult to measure or model. In the National Particulates Inventory (E.H. Pechan, 1997), emission estimates for most source categories within the fugitive dust category were derived using the particulate emission factor equations from the AP-42 database (EPA, 1995). These source categories include agricultural tilling, construction activities, paved road resuspension, unpaved roads, wind erosion and cattle feed lots. While the AP-42 emission factor approach may have some validity when annually averaged over the United States, they introduce significant uncertainties when used to estimate contributions to a single receptor on a single day (Moosmüller et al., 1998). PM-10 and PM-2.5 emissions are calculated from the TSP (total suspended particulates) emissions by applying a source category-specific (e.g., utility, paved road, wind erosion) particle size distribution factor. These factors are typically developed based on information contained in AP-42 and on engineering judgment. The chemical speciation of PM species is accomplished using source category-specific PM profiles (e.g., Shareef and Bravo, 1988) which consist of percent contribution of each chemical species within each size fraction of interest.

Sulfur dioxide (SO₂)

Almost all (97%) anthropogenic SO₂ emissions are from stationary sources (defined as all sources of emissions except highway and off-highway vehicles and natural sources). As a portion of total stationary source emissions, point sources (defined as fairly large facilities) contribute 94% of SO₂, from which the electric utility power plants

are the largest source of SO₂ emissions, contributing 67% in the United States Inventory (Saeger et al., 1989). The non-utility sources in the inventory include industrial combustion, non-ferrous metal smelting, iron and steel industry, petroleum refineries, oil and natural gas production, pulp and paper, and cement manufacturing. Industrial combustion includes all industrial fuel use but combustion of bituminous coal results in most SO₂ emissions in this category. Non-ferrous metal smelting includes primary copper, primary and secondary lead, primary zinc, and primary aluminum smelting. SO₂ emissions in petroleum refineries result from processes such as catalytic cracking, flaring, process heaters, and sulfur recovery systems.

The activity rates for most SO₂ sources are well known due to detailed production records that are maintained by individual facilities and submitted to local/state/federal regulatory agencies as part of permitting requirements. Emission factors characterizing the SO₂ content in the fuel is also quite reliable. The uncertainty in SO₂ emissions arises from the source-to-source variability that is not always captured in the emission factors that are universally applied to all sources within a source category.

Nitrogen Oxides (NO_x)

The anthropogenic NO_x emissions in the United States inventory (Saeger et al., 1989) come from mobile sources (40-45%), power plants (30-35%), and other industrial sources (20%). About half of the NO_x emissions associated with mobile sources come from the light-duty gasoline trucks and cars and approximately one-quarter are from heavy-duty gasoline and diesel vehicles. A significant fraction of NO_x emissions includes biomass burning, lightning and soil emissions. In the United States, most of the NO_x associated with biomass burning comes from wildfires. Lightning can be a significant source of nitric oxide (NO) due to the high temperature conversion of nitrogen (N₂) and oxygen (O₂) to nitric oxide (NO). NO_x is produced in soils by the microbial processes of nitrification and denitrification and by several chemical reactions that involve nitrate. The variables that include NO_x emissions from soils include soil temperature, moisture content, soil nutrient level, vegetation cover, fertilization and climate.

Like the anthropogenic sources of SO₂ emissions, the emission estimates of NO_x from stationary sources are quite reliable in terms of the operating rate data and emission factors. The largest uncertainties in NO_x emissions come from estimating NO_x from mobile sources which account for nearly one-half of total NO_x emissions in the U.S. inventory and more in some urban airsheds. Mobile emission estimates are generated by multiplying an estimate of vehicle activity by an emission factor specific to the process by which emissions are generated, e.g., tailpipe, evaporative, running loss (Maldonado, 1991). Vehicle activity data used to generate the emission estimates are typically generated by transportation planning models. However, the transportation planning models are primarily designed and used by transportation analysts to evaluate the effects of increased development on roadway level-of-service and to determine roadway capacity needs for local and regional planning (CARB, 1993). Most transportation models produce activity estimates only on an average daily basis and only for average weekday conditions. In reality, however, the levels of vehicle travel vary significantly by hour throughout the day and from week-days to week-ends as well. The inability of these models to resolve the temporal variation in mobile emissions could be a large source of uncertainty.

Volatile Organic Compounds (VOC)

A large amount (40%) of the anthropogenic VOC emissions in the United States inventory (Saeger et al., 1989) comes from mobile sources. Solvent emissions resulting from evaporation of organic solvents and application of surface coatings are distributed across a broad group of sources and comprise 32% of total VOC emissions. Other sources such as industrial manufacturing activities and fuel combustion comprise the rest (28%). In the mobile source category, emissions from light-duty cars and trucks make up the largest contributing fraction. The mobile source hydrocarbon emissions result from incomplete combustion of fuel and lubricating oil in the exhaust and gases that leak from the engine, vaporization of fuel as a result of the heating of the fuel tank, vaporization of fuel from the heat of the engine after it has been turned off, vaporization of fuel from the fuel system while the vehicle is operating, fuel losses due to leaks and diffusion through

containment materials, and fuel vapor displacement as a result of filling fuel tanks. The vehicle activity data used to estimate mobile source emissions are uncertain as discussed above.

Organic solvent utilization accounts for the largest anthropogenic, non-mobile source of VOC emissions. These emissions result from the use of organic solvents in the dry cleaning industry, in metal degreasing, in cutback asphalt paving, and in a variety of consumer and commercial product manufacturing. The solvent emissions from surface-coating-related industries include automotive furniture and appliance manufacturing, painting, and metal and plastic fabrication industries. The sources described above are generally numerous and small and, therefore, very cumbersome to track individually in an emission inventory. While the emissions from these sources are estimated individually, they are grouped together as area sources in an emission inventory. The typical cutoff to distinguish point and area sources in an emissions inventory is 10 tons/year based on annual emissions. Emissions from area sources are estimated either using the emission factor approach (Equation 3-1) or a material balance method. The material balance method is more appropriate for a solvent evaporation source. This method assumes that all solvent consumed by a facility (or in an area) is evaporated to the atmosphere and can be estimated using production or usage data. In addition to the uncertainties in emission factors discussed earlier, other sources of uncertainties in estimating emissions from area sources include exclusion of sources, double counting of emissions and lack of adequate spatial resolution due to lumping of various sources.

Each point and area source category of an emissions inventory is assigned a speciation profile (e.g., Shareef et al., 1988) that contains the weight percent breakdown of the individual species that make up the profile. These profiles are used to calculate the amount of each species from the total VOC emissions for each source category. Since the speciation requirement for VOC emissions may change depending on the chemical mechanism used in a particular application, it is desirable to keep speciation as flexible as possible. To achieve this flexibility the VOC emissions are speciated into a species list that is more comprehensive than the list of species needed for most chemical mechanisms available today (e.g., CBM4, RADM, SAPRC). For example the PSPLIT module of the NAPAP inventory divides the hydrocarbon emissions into 640 discrete species. This

comprehensive list is then reaggregated into classes based on the requirements of the selected chemical mechanism.

About 98% of the annual natural emissions of total VOC in North America are emitted from vegetation. Emissions from these sources are typically estimated using a numerical model known as the Biogenic Emission Inventory System (BEIS). The earlier versions of the model, BEIS version 1 (BEIS1) (Pierce and Waldruff, 1991) and BEIS version 2 (BEIS2) (Geron et al., 1994) were quite crude in their characterizations of biogenic emissions and chemical speciation. For example, BEIS1 used four categories to represent VOC: isoprene, α -pinene, other monoterpenes, and unidentified biogenic compounds. The current version of BEIS, BEIS3, provides emission estimates at a spatial resolution of 1 km², for 35 individual VOC (isoprene, 2-methyl-3-buten-2-ol, 18 monoterpenes, 11 oxygenated VOC and 4 light hydrocarbons) and 3 lumped VOC categories. The BEIS model calculates emission estimates using an approach similar to Equation (A-1), with the individual terms representing the following: EF is the landscape average emission factor, O is the activity factor and (1- η) is the landscape escapes efficiency (i.e., the fraction of emitted biogenic compounds that escape the canopy). EF is calculated from estimates of plant species composition and species-dependent emission factors. The activity factor, O, accounts for the influence of environmental conditions, e.g., the effect of temperature on emissions. While the chemical speciation in biogenic emission inventories has significantly improved since the earlier versions of the BEIS model, the current speciation of BEIS3 places an emphasis on O₃ precursors, e.g., isoprene. The precursors of PM, especially those forming secondary organic aerosols are poorly represented in current biogenic emission models. For example, BEIS3 lumps other monoterpenes and sesquiterpenes into one “lumped VOC” category. This simplification can be a serious limitation in PM and visibility modeling.

NH₃

Agricultural sources (i.e., livestock operations and fertilizer application) make up approximately 90% of ammonia emissions in the U.S. national inventory (E.H. Pechan, 1994). In regional emission inventories, other source categories also contribute a

reasonable amount, e.g., sewage treatment facilities in the San Joaquin Valley (SJV) inventory (STI, 1998). Currently, ammonia emissions for most source categories are calculated by multiplying emission factors and activity data. The emission factors are based on experimental data or best engineering judgement. Historically, the NH_3 emission factors for most source categories are obtained from the AP-42 (EPA, 1995) database. These emission factors are quite uncertain in some cases, and can vary over several orders of magnitude (e.g., fertilizer manufacture). The activity data for most sources of NH_3 emissions are typically obtained from survey responses. For example, in the U.S. inventory, the activity data for livestock NH_3 emissions were obtained from the 1992 Census of Agriculture (BOC, 1995). This data base has county-level estimates of number of heads for the following livestock: cattle and calves, hogs and pigs, poultry, sheep, horses, goats and minks. The activity data for fertilizer application were obtained from the Commercial Fertilizers Data Base (TVA, 1990). This data base includes county-level usage in 6-month increments of over 100 different types of fertilizers including those that emit NH_3 .

Due to the importance of NH_3 in the formation of secondary PM, a pilot-scale field study was conducted in the SJV to develop better emission factors for NH_3 from a dairy, a farm plot, and a wastewater treatment plant (Fitz et al., 1997). Such focused studies allow for a calculation of NH_3 emissions for cases where special circumstances may have influenced the activity of a given source, such as unusual meteorological patterns or variation in management practices. Similar studies have been performed in the Los Angeles area (Fraser and Cass, 1998).

Overall inventory

Constructing an emission inventory for an Eulerian air quality model application can be viewed as involving two steps: (1) emission estimate calculation for each pollutant (i.e., PM, SO_2 , NO_x , VOC, NH_3) for individual sources (e.g., power plants) or source category (e.g., mobile sources) and (2) spatial, temporal and species allocation of the emission estimates in a manner consistent with the formulation of the air quality model. The calculation of emission estimates is based on Equation (3-1) and is a function of

three parameters: emission factor, activity rate and control device efficiency (or landscape escape factor). Few measurements of these three parameters are made at representative sources within each source category. These measurement data are then used to quantify the parameters which are then applied to all sources within a source category. In theory, a perfect inventory, within measurement uncertainties, can be generated by collecting continuous measurement data at all sources of emissions. However, it is not practical to do so, and, therefore, the overall quality of the emission estimates, is determined by how well the parameters represent all sources in a source category.

In the second step, surrogate variables are typically used to spatially, temporally and chemically resolve the emission estimates so that they are consistent with the requirements of the air quality model. Spatial allocation of point sources is quite accurately known from the plant-specific location data but the spatial allocation of area sources is usually accomplished using surrogate variables such as population or energy consumption, that might not properly characterize the variability of sources in a given source category. Similarly, temporal surrogate variables used to obtain hourly emission estimates might not reflect the real-world conditions (e.g., weekend versus weekday conditions for mobile sources). The chemical resolution of the emission estimates is typically governed by the chemical mechanism used in the air quality model.

A.5.2 Evaluation of Emission Inventories through Measurements

Mobile emissions

Emissions of CO, VOC, NO_x, and PM from mobile sources are an important source of air pollution in many urban airsheds. Tunnel studies using infrared remote sensing (Stedman et al., 1994) provide an excellent means of validating emission estimates from mobile sources (Harley et al., 1997). Concentration of VOC, CO, NO_x and PM can be measured at both the upwind and downwind portals of the tunnel and the emissions rate can be calculated based on their difference. Measured emission rates in tunnel studies in California (Pierson et al., 1990), eastern United States, (Robinson et al.,

1996) and Canada (Gertler et al., 1997) have been compared to predictions from emission factor models. The main advantage of tunnel studies is that they can be used to characterize emissions from a large random sample of on-road motor vehicles. The disadvantage is that tunnel measurements represent primarily mobile emissions from running losses and do not account for influence of cold start or evaporative emissions or the effect of high speed and heavy acceleration driving conditions. Furthermore, tunnel studies, as opposed to laboratory testing, cannot be used for controlled experiments to understand the effect of individual parameters, e.g., fuel composition, vehicle air conditioning.

Another area of improvement with respect to the mobile source emissions is to obtain better vehicle activity data than those provided by transportation models. The vehicle activity data should include temporal variability in travel activity (summertime versus wintertime, week-day versus week-end, peak morning hours versus afternoon hours), vehicle type distribution (automobile, light-, medium-, or heavy-duty truck) and type of road (freeway, arterial, collector or local). Such a high resolution of vehicle activity data was collected during the 1990 San Joaquin Valley field study (CARB, 1993). Vehicle counts were collected at several locations in the study region during the summer of 1990. These counts were made during mid-weekdays, as well as for Friday, Saturday and Sunday to develop day-of-the week correction factors. Hourly counts were also maintained during episodic days for the development of time-of-day distributions. Seasonal correction factors were developed by assembling count data for some days of the week during spring and fall months. To develop the vehicle type distributions, vehicle classification counts were kept each day of the week during the episode period for all hours of the day. The above database contained roughly 100 days of count data covering 220 locations. To supplement these data, classification counts were also made at several locations during the 1990 summer field study using either manual, mechanical and videotape techniques.

Stationary Sources

Gaseous pollutants emitted from a significant number of large stationary sources in the United States are directly measured using continuous emissions monitoring systems (CEMS). Primary PM emissions are not measured on a routine basis. Data from the CEMS are generally superior to estimates made using emission factors or other estimation technique. This is to be expected since CEMS provides measurements of in-stack emissions levels, whereas emission factors were based on a small number of stack testing on plants that were not necessarily representative of the entire population of sources. Currently, all electric-utility power plants with nameplate capacity greater than 25 MW have installed CEMS that measures in-stack levels of SO₂, NO_x, CO₂ and stack gas volumetric flow rate. The CEMS usually consists of an emission analyzer, a diluent analyzer, and software for reporting and manipulating the measurements. The pollutant emission rates are estimated from CEMS measurements of pollutant concentrations (in ppm) and dilutant concentrations (%) using standard algorithms. Emission measurements from CEMS have had some system problems in some cases associated with calibration of flow meters, missing data substitution protocols, software errors and use of monitoring equipment outside the design range. However, these system-level problems are expected to decrease as the users gain more experience with the system.

Area Sources

Direct measurements of area source emissions such as CEMS for point sources, is not practical because (1) there are numerous individual sources and (2) activities associated with these sources are often hard to determine or are, at best, arbitrary. Techniques for estimating area source emissions from ambient data or remote sensing of emissions sources are in the experimental stages of development. Area source emissions are typically estimated using a top-down approach, i.e., allocating an operating rate that is known for a large area, such as a state or nation, to smaller areas and then applying an emission factor. A bottom-up approach, on the other hand, involves collection of locally available operating data through a comprehensive survey effort. While bottom-up

inventories are resource intensive, they are capable of providing better spatial and temporal resolution and are more appropriate for area source emissions. For example, a day-specific VOC and NO_x emissions inventory was generated from numerous oil production sources in the San Joaquin Valley by gathering questionnaires containing daily operating data and collected by means of a postal survey (CARB, 1992).

Micrometeorological techniques can also be used to measure emission fluxes from biogenic area sources (Businger and Delaney, 1990). These techniques require the measurement of fluxes and gradients of one passive scalar such as heat, water vapor or carbon dioxide using fast response sensors. The measurements are then used to calculate a transfer coefficient K, which is assumed applicable to all passive scalars. The transfer coefficient and the concentration gradient can be used to calculate the above-canopy biogenic VOC fluxes. This technique has been used to calculate fluxes of chemically reactive species (Galmarini et al., 1997). The technique has limited use in areas with even moderately complex terrain.

Inverse modeling can also be used to estimate emissions from area sources. Inverse methods use existing air quality data and models of the transport and transformation processes to infer what the inputs would have to be in order to best fit model predictions to measured concentration. The techniques vary from simple approaches like source-receptor models (e.g., Cass and McRae, 1983) to more sophisticated Kalman Filter based approaches (e.g., Hartley and Prinn, 1993; Mulholland and Seinfeld, 1995).

Overall Inventory

The overall emission inventory needs to be evaluated using independent data. The evaluation must address the absolute amount, relative composition, spatial pattern and temporal distribution of the emissions. Several methods have been used in the past for an overall inventory evaluation. These methods include both top-down and bottom-up approaches and include the following:

- Reconciliation with ambient data

- Ground truth verification
- Modeling

Each of these methods is briefly discussed below.

Reconciliation with ambient data

Comparison of ambient data and emission inventories provides a quantitative evaluation of the relative composition of emissions. It is a form of top-down inventory evaluation. During the SCAQS-87 study comparisons of CO/NO_x ratios and VOC/NO_x ratios in the ambient air were made to evaluate the relative amounts of CO, VOC and NO_x emissions in the SoCAB (STI, 1991). The SCAQS VOC data included a comprehensive set of individual C1-C12 hydrocarbon and C1-C7 carbonyl concentrations at several locations and aircraft measurements of VOC between 500 and 800 m above ground. This extensive set of speciated VOC data made it possible to compare the relative amounts of individual organic species and species groups measured in the ambient air with the VOC speciation of the inventory. The largest uncertainty in comparisons between ambient data and emission estimates is the fact the ambient measurements are influenced not only by fresh emission emitted near the source, but also by transport and chemistry. These uncertainties can be minimized by making the comparison during times when emission rates are high and the influence of other factors are low, e.g., low wind speeds and negligible chemistry.

Ground truth verification

This method involves techniques that make direct comparisons between emissions estimates and some other known quantity that is related either directly to the emission source or indirectly to the underlying process that results in emissions (Mobley and Saeger, 1993). In contrast to the comparison against ambient data discussed above, this technique represents a bottom-up form of inventory evaluation. While this method can be resource intensive, it often provides a powerful method to evaluate the absolute form

of emissions. Ground truth verification techniques include detailed manual surveys of sources known to contribute significant emission magnitudes and monitoring studies at individual facilities. The use of CEMS would be an example of ground truth verification by monitoring at the stack.

Modeling

Both source- and receptor-oriented models can be used to evaluate emission inventories. In receptor modeling, ambient data and the chemical composition profiles from selected sources are used to assess the contributions of different sources to the observed concentration of pollutants. The relative contributions of sources provided by receptor modeling can then be used to evaluate the emission inventories with some appropriate assumptions on transport and removal. Source-oriented three-dimensional models, on the other hand, attempt to treat all relevant atmospheric processes including emissions, transport, dispersion, chemistry and deposition. Assuming that we have included a comprehensive treatment of the relevant governing processes in the model and that the uncertainties in other model inputs (e.g., meteorology) are relatively small, it is reasonable to attribute deviations between model predictions and observations to uncertainties in the emission inventories. The model can also be used as a sensitivity tool to test known biases in the emission inventories; For example, Fujita et al. (1992) compared CO/NO_x and VOC/NO_x ratios in the emissions inventory and ambient concentrations in the Los Angeles basin. They concluded that the observed ratios were about 1.5 and 2-2.5 times greater, respectively, than the ratios in the emission inventory. Lu et al. (1997) used the SMOG modeling system to suggest that the emission inventory underestimated VOC emissions. Such approaches cannot be used as absolute tests of the emission inventories since there are many other sources of uncertainties in a model. Nevertheless, a large discrepancy between model predictions and observations may be pointed at the emission inventory, thereby suggesting the use of other techniques to better evaluate the emission inventory.

A.6 Atmospheric Deposition

A.6.1 Dry Deposition

Dry deposition refers to the transfer of airborne material, both gaseous and particulate, to the earth's surface, including soil, water, and vegetation, where it is removed. The dry deposition process consists of three distinct steps: (1) turbulent diffusion of the material through the surface layer to the immediate vicinity of the surface, (2) surface transport of the material through the laminar sublayer next to the surface to the absorbing component of the surface, and (3) removal of the material at the surface sites. Due to the complexity of the process, dry deposition is typically represented parametrically using the deposition velocity (v_d), which is related to the flux of the material to the surface:

$$F_d = v_d c \quad (\text{A-2})$$

where F_d is the deposition flux, and c is the concentration in the bulk gas phase.

Collection of deposited material on a surrogate surface is generally considered not to be a very accurate method because deposition is a strong function of the surface type for most chemicals. Therefore, techniques that are based on micrometeorological measurements are recommended. Such techniques take advantage of the atmospheric mixing that integrates the different fluxes that occur over the various leaf and soil surfaces present in a particular canopy, thereby yielding values representative of the entire underlying surface. Two micrometeorological techniques that have been widely used to study the dry deposition of gases and particles are the gradient method and the eddy correlation method.

We discuss below these two methods and their application to gases and particles of interest in the PM formation, including ozone, NO, NO₂, SO₂, ammonia, PM-2.5, and PM-10. Chemical sensors suitable for these techniques are also briefly discussed.

Gradient Method

For a homogeneous and stable atmosphere, the vertical fluxes (F) of gases for a given layer can be determined as the product of the eddy diffusivity (K) and the concentration gradient measured:

$$F = -K \frac{\Delta c}{\Delta z} \quad (\text{A-3})$$

where $\Delta c = c(z_2) - c(z_1)$ and $\Delta z = z_2 - z_1$, the concentration and height differences at two sampling points. The determination of turbulent diffusivity presents a major difficulty for the application of this method. Horváth et al. (1998) used Monin-Obukhov's similarity theory and universal functions to determine K ; however, such procedures can not be applied to complex surfaces such as forests. Alternatively, the Bowen Ratio Method (e.g., Lindberg et al., 1995) assumes that

$$F = F_s \frac{\Delta c}{\Delta q} \quad (\text{A-4})$$

where $\Delta \theta$ is the difference in potential temperature at the two levels, and F_s is the vertical flux of latent heat. Lindberg et al. (1995) relaxed the assumption that the transport characteristics of heat and scalars are similar by using another scalar, such as CO_2 or H_2O vapor concentration, as a reference. The flux of latent heat or chemical compound can be determined directly by eddy correlation measurements (see below).

Horváth et al. (1998) applied the gradient method to estimate the dry deposition velocities of NO , SO_2 , and O_3 above short vegetation (grass, wheat, and mustard plants) under both stable and unstable conditions. They determined the deposition velocity of O_3 and SO_2 to be $0.05\text{-}0.07 \text{ cm-s}^{-1}$ and $0.19\text{-}0.20 \text{ cm-s}^{-1}$, respectively. NO emission was observed.

Eddy Correlation Method

Eddy correlation is considered by many to be a relatively direct method for determining dry deposition. The basic idea is that the flux of a scalar can be determined as its covariance with the vertical component of wind, i.e.,

$$F = \overline{c' w'} = \overline{(c - \bar{c})(w - \bar{w})} \quad (\text{A-5})$$

where the overbar denotes an averaged quantity and the prime denotes fluctuations around the mean value. In essence, the downward flux is large when downward fluctuations of wind are associated with high concentrations, and vice versa. The covariance represents the vertical component of the net flux at the height of the measurements; therefore, non-divergent and stationary atmospheric conditions are needed to infer the surface flux (see also Pederson et al., 1995).

Traditionally, eddy correlation measurements were made on fixed instrumentation towers. For example, diurnal profiles of deposition velocities for ozone were measured over three types of surfaces in the San Joaquin Valley, CA (Massman et al., 1994). There is a large body of literature for deposition flux measurements of trace gases, such as SO₂, NO, NO₂, O₃, CH₄, etc. Gallagher et al. (1997) measured the deposition fluxes of sub-micron particles onto a forest surface using the eddy correlation method. Particle concentrations were measured with an optical counter. They found that the deposition velocities can be as large as 1 cm-s⁻¹ for particles in the size range of 0.3 to 0.5 μm.

Eddy correlation measurements can also be made from aircraft and other moving platforms. Although it is harder to meet the atmospheric conditions for valid inference of surface fluxes, aircraft measurements can effectively sample different surface types within the domain. Hubbe and Pederson (1994) claimed favorable comparisons between aircraft and ground based measurements of O₃ and CO₂ deposition fluxes in the San Joaquin Valley, CA, over cotton, grape, and grass surfaces.

Chemical Sensors

The key requirement for determining dry deposition fluxes using the gradient method is obtaining accurate measurements of the concentrations of the chemical species of interest. Measurement sensitivity may be increased by increasing the averaging time of measurements, as long as the stationarity criterion of the atmosphere is satisfied. However, the requirements for accurate determination of fluxes using the eddy correlation method are more stringent. In addition to a fast response anemometer (e.g., a sonic anemometer with a frequency response of >10 Hz), chemical sensors with a frequency response of at least 0.5 Hz are also required. A 5 to 10 Hz response time is preferable for aircraft measurements. This excludes the application of the eddy correlation method to species such as HNO_3 and NH_3 for which fast response measurements are not easily available. Table A-12 compiles some chemical sensors that can be used to measure deposition fluxes of species relevant in the PM issue. Other chemical sensors, as described in Sections A.1 and A.2 may also be adapted for measuring fluxes (see also Pederson et al., 1993).

A.6.2 Wet Deposition

Wet deposition to surfaces and the ground is a significant removal process for atmospheric pollutants (Waldman and Hoffmann, 1987). Wet deposition includes precipitation in the form of rain and snow, fog, intercepted clouds with mountains, and dew formation. The sections below briefly discuss deposition of atmospheric pollutants by these removal processes.

Precipitation

The amount of precipitation in the form of rain or snow has been monitored routinely for many years. These results are usually obtained by standard rain gauges or by measuring the depth of snow that has fallen on the ground. However, these methods do not provide samples that can be used for chemical analysis of the collected

Table A-12. Summary of Chemical Sensors and Micrometeorological Techniques used to Measure Deposition Fluxes (adapted from Baldocchi et al., 1988).

Chemical Species	Sensor	Technique ^(a)
O ₃	Chemiluminescence	EC
	Bubblers	G
NO ₂	Chemiluminescence	EC
	Luminol	EC
SO ₂	Flame photometry	EC
	UV Absorption	EC
	Bubblers	G
HNO ₃	Nylon filters	G
NH ₃	Absorption traps	G
PM	Optical particle counter	EC

(a) EC: Eddy Correlation Method; G: Gradient Method

sample, as they are usually left open allowing for contamination due to dry deposition. Slightly more sophisticated samplers, and ones which are still in use today, use buckets with automated covers (Eaton and Estes, 1984; Topal and Ozdemir, 1986). An electronic sensor is used to open and close the bucket that is lined with a clean plastic bag. Samples are usually collected on a weekly basis with chemical analysis performed sometime later in the laboratory using standard techniques. More sophisticated samplers can collect samples of shorter duration, that is, multiple samples during a single rain event with storage of the sample at reduced temperatures (Seymour and Stout, 1983; Coscio et al., 1982). Kronmiller et al. (1990) describe a sampler that also measures pH and conductivity in real-time, along with preserving each sample fraction in clean containers maintained at reduced temperatures in a refrigerator, which is part of the sampler. Chemical analysis of the samples can be done in the same manner as with the fog and cloud samples. However, stabilization of labile species would require an operator on the site during sample collection. The deposition can be determined by the amount of water collected, the sampling time, and the size of the collector's inlet.

Dew, Fog, and Clouds

Determining the deposition of dew and fog to the surface at ground level and interruption of clouds by terrain at higher elevations is typically performed using two approaches. The first approach is to use exposed surfaces such as leaves or a surrogate surface to measure the amount of water collected by that surface over a given time period (Pierson et al., 1988; Collett et al., 1998a). If collected carefully the sample can be analyzed chemically as described above in Section A.2 for the fog measurements. The second approach is to determine the deposition from samples collected using a fog or cloud collector as described above in Section A.2. Accurate determination of fog or cloud deposition by the second approach requires detailed knowledge of the drop size spectra. This can be obtained using, for example, the size fractionating-CASCC and the PMS-CSASP (Collett et al., 1998a). The flux is calculated from the liquid water content, the mass fraction (if size fractionated samples were collected), and the deposition velocity of the droplet. Deposition as a function of drop size is important since the

chemical composition of fog varies as a function of particle size (Collett et al., 1997) and since larger droplets are removed faster than smaller droplets, thus enriching the fog in fine droplet chemical components (Collett et al., 1997; Collett et al., 1998a). Deposition of chemical components to the surface is determined from the measurement of the chemical constituents

A.7 Measurements of Atmospheric Visibility

Instruments and techniques are available for measurements of various components of atmospheric extinction. Such data are needed to characterize visibility and to provide information for evaluating visibility models and the optical modules of those models. Instruments or techniques that are readily available measure the radiance or luminance, I (and hence the apparent contrast, C); the light extinction coefficient b_{ext} ; the scattering coefficient b_{scat} ; and the particle absorption coefficient b_{ap} . Other instruments that measure a portion of the scattering of light, typically in the backward direction (i.e., back toward a light source) are used for meteorological and aviation purposes, but are poorly suited for air pollution-related visibility assessment and thus will not be discussed here.

Techniques that are in current use for measurement of the air pollution-related optical properties of the atmosphere are described below. The methods discussed here are ones for which there are well-established procedures or commercially available instruments, and that are well suited for routine measurements. Specialized research techniques that require highly skilled operators are not addressed here.

The first several methods discussed below measure properties over a path through the atmosphere, and thus give an average over a path, while the later methods determine properties at a given location. This difference has to be considered when comparing measurement results. In a sense, a long-duration measurement at a point is analogous to a short-duration path measurement along the wind direction, because the long-term sampling integrates over the air mass that the wind carries past the sampling point during the duration of sampling. For example, a one-hour of sampling in a 5 km/h wind integrates over a 5 km long sample, which is analogous to an instantaneous measurement over a 5 km

path. On the other hand, a short-term measurement at a point reflects an instantaneous measurement of a local property.

A.7.1 Radiance and Luminance

Teleradiometers and telephotometers

These instruments, which consist of a telescope and a photocell, measure the amount of light energy arriving from an illuminated object, and thus determine its brightness, I . Teleradiometers measure the radiance, which is the energy at a one or more given wavelengths of light. Telephotometers measure the luminance, which represents the energy integrated over the spectral response of the eye, with the energy at each wavelength weighted with the relative sensitivity of the eye at that wavelength (the photopic response).

Information about the brightness of a scenic element and the horizon sky behind it can be used in Equation (1-1) to deduce the contrast and then in Equation (1-3) to infer b_{ext} for the wavelength spectrum represented by the measurements, the initial contrast, C_0 , has to be determined by making measurements of the scenic element at a close distance (see Equation 1-3) or on a very clear day (Rayleigh b_{ext}) with identical illumination as that at the time of interest (The equations referenced here are in the main body of the report). Accurate determination of the correct C_0 at any instant is difficult in practice, and therefore b_{ext} determinations by this method tend to have relatively large uncertainty.

Radiance and luminance measurements by teleradiometers, telephotometers, and photography (see below) were in common use in the 1980's to determine apparent contrast and the extinction coefficient. Teleradiometers designed specifically for atmospheric visibility instruments were manufactured by Meteorology Research, Inc. They are no longer manufactured and the company no longer exists. For the purposes of determining atmospheric extinction such instruments have been supplanted by techniques that measure components of extinction directly, rather than the effects of extinction on the appearance of a scenic element. Teleradiometers and telephotometers are still used for visual perception research; such instruments are available from optical instrumentation suppliers.

Photography

Measurement with a densitometer of the densities of scenic elements in a photographic image provides the same information about scenic element radiances or luminances that is provided by the teleradiometer/telephotometer technique. The densitometer determination of information from a spot on the film is analogous to the measurement by a teleradiometer or telephotometer of the brightness of the corresponding spot in an actual scene. Because the response of the film varies with wavelength and the image density not linearly related to the amount of incident light, a photograph of standard color and density charts needs to appear on each roll of film.

The photographic technique (sometimes referred to as sensitometry) requires no complex instrumentation in the field and can be fully automated, and therefore is readily used in remote areas. It has the same technical weaknesses as the teleradiometric/telephotometric approach and is slightly less accurate and precise because of the additional steps of recording an image on film and developing it (Seigneur et al., 1984; Johnson et al., 1985).

Complete camera systems designed for documenting visibility conditions are available from Air Resource Specialists in Ft. Collins, CO. These camera systems are used in many Class I PSD areas in the federal IMPROVE (Interagency Monitoring of Protected Visual Environments) program, although quantitative analysis of the film image is no longer performed. Spot densitometers for measuring the image density are available from several photographic equipment manufacturers. They have been increasingly replaced by film scanners that digitize the entire image for computer analysis.

Digital cameras could be used advantageously for this purpose since the step of digitizing the film would be eliminated, thereby reducing the uncertainty of the measurement. Digital cameras have not yet been applied to atmospheric visibility measurements because reasonably-priced cameras that can provide sufficient resolution are just beginning to appear on the market.

A.7.2 Total Extinction

Transmissometers

A transmissometer is a teleradiometer that measures the light arriving from an active light source that has been placed at a distance. Typically for the purposes under discussion here, the light source (an incandescent lamp) is located at a distance of several kilometers. Alternatively, the light source can be collocated with the receiver and a retroreflector several kilometers away can be used to produce a path. This instrument measures the attenuation of the light from the source, from which the average light extinction, b_{ext} , along the path can be determined from Equation (1-4). Measurements are made instantaneously, although typically several measurements over an hour are used to construct a one-hour average.

As with the need to determine C_0 when using Equation (1-3) for determining extinction, Equation (1-4) requires determining I_0 . This is usually done by placing the source and receiver at a relatively close distance. Because the output of real lamps drifts some with time, errors are introduced in the b_{ext} determination unless I_0 is measured frequently. This is typically not practical, and so some uncertainty is introduced into typical b_{ext} determinations.

The transmissometer measures not only the attenuation of light by the aerosol, but also any attenuation of the source brightness due to broadening of the beam by atmospheric turbulence and alteration of the brightness by diffraction. Both of these artifacts will weaken the beam and thus cause the instrument to overestimate the extinction that would be attributed to air pollutants alone.

A transmissometer that is designed for air-pollution related atmospheric extinction measurements is manufactured by Optec, Inc. of Lowell, Michigan. This instrument is used in the federal IMPROVE network.

A.7.3 Scattering due to Particles and Gases

Integrating nephelometer

An integrating nephelometer determines light scattering by particles and gases, b_{scat} , by measuring the amount of light that is scattered out of a volume of aerosol over a short (tens of centimeters) path. Nephelometer measurements are continuous, with a temporal resolution of the order of a second to a minute, depending on the design. The instrument is calibrated using particle free air for the Rayleigh scattering point and a halocarbon gas with known scattering for an upscale point.

The geometry of the instrument is such that the optical signal is proportional to the integral of light scattering over (ideally) the full 180° from forward scattering through back scattering (hence the name, integrating nephelometer), and thus it is intended to measure the total light scattered by the aerosol.

In reality, the geometric configuration of real nephelometers does not allow for measurement of scattering in the few degrees around the most forward (0°) and backward (180°) directions (the truncation error). Calibration of the nephelometer using gases compensates for this when the instrument is used to measure light scattering by air, but the correction is incomplete for measurements of particles, which tend to scatter more light in the forward direction than do gases. Nevertheless, the truncation error is quite small (a few percent) for the typically submicron fine particles. The truncation error becomes large for particles larger than a few micrometers, however, and the instrument measures only about half of the scattering from coarse particles of around $10\text{ }\mu\text{m}$ diameter and larger.

Commercially-available integrating nephelometers come in two configurations. One configuration, reflected in instruments from Meteorology Research, Belfort Instruments, Radiance Research, and TSI, measures the air drawn by a fan into a dark, enclosed optical chamber. A different configuration, reflected by instruments from Optec, has an optical chamber that is open on one side to the ambient atmosphere.

The biggest uncertainties of the nephelometric measurements derive from the need to draw the air into an enclosed or partially enclosed sampling chamber. Because of the light source at that chamber, the sampled air is heated slightly, by about 0.5° to 1° C in the

semi-open designs and by several degrees in some of the enclosed configurations. This heating alters the relative humidity of the air and therefore, when the particles being sampled are hygroscopic, dries them out slightly and thus may reduce their scattering. Configurations with sampling ducts also may lose larger particles in the ducts and therefore also underestimate the scattering for this reason.

Consequently, because of sample heating, duct losses, and truncation error, light scattering measurements of ambient aerosol tend to understate the true scattering to some degree.

The drying of particles by the nephelometer can be used to advantage in some situations. By intentionally heating the aerosol enough to dry it below its deliquescence point, the nephelometer will measure only the scattering by dry particles, independent of the ambient humidity (although some hysteresis may limit the amount of water actually evaporating). This makes the instrument readings correlate with dry fine particulate matter concentrations and to be independent of weather. The correlation can be further enhanced if the inlet to the nephelometer contains a cyclone that excludes the larger particles that are poorly measured by the instrument; the cyclone can also be used to exclude fog droplets. This approach only works for nephelometers with fully enclosed sample chambers, however. In such modified forms the integrating nephelometer is less a visibility instrument and more an aerosol characterization instrument.

Integrating nephelometers in two designs were manufactured from 1969 to about 1982 by Meteorology Research, Inc. (MRI). The manufacture of one design was continued for some years afterward by Belfort Instruments. Many of the MRI/Belfort instruments are still in use. Currently, instruments are available from Optec, Inc. of Lowell, Michigan, and TSI Inc. of St. Paul, Minnesota. Also, Radiance Research of Seattle, Washington, has produced an updated version of the MRI/Belfort instruments. The Optec instruments, which are optimized for long-term, unattended operation outdoors, are used in the federal IMPROVE network. The TSI instruments are designed for research settings.

A.7.4 Absorption due to Particles

Integrating plate

Light absorption due to particles, b_{ap} , can be determined by collecting particulate matter on a filter and then measuring the transmittance of light through the filter in the laboratory, generally many days after sample collection. These measurements are typically made on multi-hour filter samples. The technique is called the integrating plate method because of an element in the optical system that integrates the light that passes through the sample.

Standard particulate matter samplers are used for collecting the samples. Typically, only the fine fraction (aerodynamic diameter smaller than $2.5 \mu\text{m}$) is collected through use of a size-selective sampler inlet. The laboratory equipment for the absorption measurements is specially configured by each laboratory. Two facilities that make such absorption measurements include the University of California at Davis (UCD) and the Desert Research Institute (DRI) in Reno, Nevada. UCD is making the absorption measurements for the federal IMPROVE network. The absorption determinations by the two laboratories don't always agree and there is a current debate about the correct way to make such measurements. Research techniques for determining absorption, such as photo-acoustic measurements, are being used to help resolve the discrepancy.

Aethalometer

The integrating plate light absorption method is automated in the field by an aethalometer. The aethalometer collects particles onto a spot on a filter tape and determines light absorption by measuring the attenuation of a light beam passing through the tape and the material on the filter. Measurements have a temporal resolution of a few minutes to an hour, depending on the amount of absorbing material in the air. The tape is periodically advanced to a new spot after the particulate loading has become sufficiently great to significantly reduce the transmittance.

The aethalometer is available commercially from Magee Scientific. Its measurements have been found to agree on average with filter/integrating plate

determinations by DRI, albeit with considerable point-to-point scatter (Tombach et al., 1996).

A.7.5 Absorption due to Gases

Light absorption by gases in the troposphere is due primarily to NO₂. Light is absorbed by NO₂ primarily in the violet-blue range (i.e., from about 400 to 450 nm) and an atmosphere with high NO₂ concentrations appears brown to the human eye, since most of the blue light has been removed. Measurement of light absorption by NO₂ has been conducted for NO₂-laden plumes using teleradiometry or sensitometry (See section A.7.1). For regional haze, however, light absorption by NO₂ is typically estimated from measurements of NO₂ concentrations combined with the absorption characteristics of NO₂ (Dixon, 1940). Measurements of NO₂ concentrations are described in Section A.1.

A.7.6 Summary of Instrument Performance

Table A-13 summarizes key aspects of the performance of the methods described above, when operating under field conditions. Quantification of instrument uncertainties is difficult, appropriate standards do not exist, and therefore the evaluations that have been done tend to be limited. Furthermore, instrument performance in laboratory tests tends to differ from that in the field. In many cases, expert judgment is the only guide to assessing performance. Consequently the information in Table A-13 is incomplete and the data that are there should be viewed as a qualitative guideline to instrument performance for carefully-operated instruments.

Since the sum of the integrating nephelometer and aethalometer measurements should equal the transmissometer measurements, it is possible to make measurements with an internal consistency check. But, because of the different spatial scales of the measurements and the different responses of the instruments to moisture in the atmosphere, this check does not always show full agreement. In particular, the propensity of the integrating nephelometer to underestimate the scattering must be taken into account.

Table A-13. Summary of Performance of Visibility Measurement Techniques

Method	Variable Measured	Limit of Detection	Precision	Accuracy	Potential Interferences/ <u>Artifacts</u>	Comments	References
Teleradiometer or telephotometer	I -- used to infer C and b_{ext}		$C = 0.02$ (MRI instrument)	$C = 0.01$ (MRI instrument)	Non-standard illumination (clouds)	b_{ext} determination very sensitive to C_0	Bergstrom et al., 1982
Integrating nephelometer	b_{scat}	1 Mm^{-1}	$2 - 5 \text{ Mm}^{-1}$	$\sim 2 \text{ Mm}^{-1}$ for fine particles at low RH	Sample heating, sample loss, truncation error	Different makes have differing characteristics	Tombach & Thurston, 1995; Molenaar, 1997; Day et al., 1997
Integrating plate analysis of filter sample	b_{ap}				Optical interference between filter and particles and shadowing of one particle by another	Disagreement as to correct way to correct for artifacts; all uncertainties depend on sampling duration	Lin et al. , 1973
Aethalometer	b_{ap}		$\sim 1\%$ (theoretical), 10% in practice	$< 1 \text{ Mm}^{-1}$ (theoretical)		All uncertainties depend on sampling duration	Watson et al., 1996, App. A; Tombach et al., 1996
Transmissometer	b_{ext}	$\sim 1 \text{ Mm}^{-1}$	$\sim 2 \text{ Mm}^{-1}$	$\sim 1 \text{ Mm}^{-1}$	Atmospheric turbulence and refraction; fog	Accuracy affected by lamp brightness drift	Malm & Persha, 1991

It should also be noted that all of these techniques are appropriate when the visibility effects of PM-2.5 are of interest. To the extent that visibility impairment also results from larger particles, the transmissometer is the only device that can reflect that large-particle extinction correctly.

A.7.7 Recommendations

The light extinction, scattering, and absorption measurements can be used separately to evaluate the performance of particular portions of visibility models (see Section 2.4).

Because of the effect of humidity on the scattering of light by particles, light extinction, scattering, and absorption data can be used in two ways in visibility analyses and modeling:

- The "ambient" method: Here all measurements are made so as to represent ambient conditions as well as possible. Because most nephelometric light scattering measurements begin to show errors above $RH = 70\%$, their usefulness becomes limited. Above $RH = 90\%$, all nephelometer measurements become unreliable and transmissometer measurements are influenced by clouds or fog. Furthermore, at those high humidities it is difficult to measure the RH itself accurately, which makes use of aerosol thermodynamic models less reliable. Therefore, typically, data taken above an RH of 90% are not used for air pollution aerosol optics analyses.
- The "dried" method: In this approach, the ambient aerosol is dried by passing it through a desiccator or heater, and then its scattering is measured by an integrating nephelometer. The light absorption measurements are not affected by moisture, and thus do not require the pre-treatment. These dried aerosol optical measurements can then be used for evaluating the performance of an aerosol and visibility model without need for estimating

the contribution of water to light scattering. The transmissometer can not be used in this approach because there is no way to dry the aerosol it observes.

As a variant of the second method, integrating nephelometers have been used to measure the interstitial aerosol in the presence of fog (Watson *et al.*, 1996). To accomplish this requires an enclosed nephelometer with a cyclone (typically with a 2.5 μm cut point) at the inlet. The cyclone removes fog droplets and leaves the fine particles. Of course, any effect of sample heating is reflected in the subsequent measurement of scattering unless the sample is then intentionally heated to observe the dry particles.

Ground-Based Measurements

The most commonly used configuration for ground based measurements consists of a transmissometer for b_{ext} , an integrating nephelometer for b_{scat} , and either an aethalometer or filter sampler for b_{ap} . This configuration provides some redundancy in measurements, as described above.

Since the transmissometer is the most expensive of these instruments to purchase, install, and operate, and also requires a several-kilometer sight path, it is often left out. The nephelometer and aethalometer pair can provide a good characterization of the aerosol with relatively short time resolution if the propensity of the nephelometer to underestimate scattering is taken into account.

Measurements Aloft

The only instrument described above that has been used successfully in aircraft is the integrating nephelometer of the enclosed type. Because of its fast response it has served often to characterize the spatial distribution of aerosol in aircraft surveys.

Filter sampling can be used to collect samples for b_{ap} analysis, but the low flow rates characteristic of aircraft filter samplers and the low particulate matter concentrations aloft dictate long sampling times (typically over 1/2 hour) to get sufficient sample for

analysis. Such samples can be used to describe conditions aloft, but they do not provide high-resolution information on spatial distribution (see Section A.8).

A.8 Sampling from Airborne Platforms

Chemical and meteorological measurements aloft are essential for understanding atmospheric dynamics, chemistry, and transport. Upper air meteorological measurements are now routinely conducted in intensive field measurement programs using remote sensing from surface based instruments, such as radar wind profilers, doppler acoustic sounders, or balloons launched from the surface and tracked either optically or by radio. These upper air meteorological measurements are described in Section A.4. This section addresses gas- and particulate-phase measurements from aloft sampling platforms.

There are basically five platforms that can be used to measure chemical components aloft. These include the use of tethered balloons, free balloons (or sondes), tall towers (typical maximum height is 615 m, e.g., the Boulder tower), aircraft, and satellites. Each of these platforms provides different options for measurement programs, and their use depends on study objectives, cost, and species of interest. Tethered balloons and towers typically represent point measurements at some height above the surface; although both can provide some vertical resolution if multiple systems are used at different heights. However, spatial resolution is limited to one point per system. Towers also are limited in height (maximum radio tower heights are in the range of 400 m, see for example the tower used in IMS95, Collett et al., 1997) and in location, as there are few tall radio towers available in a given area. Building a temporary tower is an option; it is however expensive and limited in vertical height (e.g., \$100,000 for a 100 m tower installed for one year; Neff, NOAA, personal communication, 1998). Towers and tethered balloons allow for sampling at one height for extended time periods, thus allowing the boundary layer to move back and forth across the sampling location if placed correctly. Samples collected by free balloons, on the other hand, provide considerable vertical resolution and extended heights, but sample a given point in space only once. Satellites have been used widely for stratospheric measurements, but even there often lack the sensitivity needed for small scale resolution, in both the vertical and

horizontal dimensions, as well as analytical sensitivity (Brune and Stimpfle, 1993). Aircraft, while expensive to operate for long-term programs, have many advantages over these other platforms in regional field programs, and to date, aircraft are the most widely used platforms for chemical measurements aloft.

Requirements for sampling aloft aboard a moving aircraft platform are different and typically more stringent than those for monitoring at a point location at the surface. Nevertheless, measurement methods have been developed or modified to meet many of these requirements. Some specific examples are provided in Daum and Springston (1993) for the measurement of O_3 , SO_2 , NO_x , CO , H_2O_2 , PM , and cloud water liquid water content. Parrish and Fehsenfeld (1998) also describe examples of methods used aboard aircraft and specifically present brief summaries of methods intercomparisons that have occurred aboard aircraft platforms. As with surface measurements, some of these pollutants require the collection of time-integrated samples with subsequent chemical analysis in the laboratory or even aboard the aircraft, while other methods are continuous. Time-integrated methods include the use of filter packs to collect PM and precursor gases where the collected PM can be analyzed for chemical constituents at a later time, the collection of cloud water or precipitation using methods similar to the fog and cloud collectors described in A.3, and the collection of grab samples using canisters, cartridges, or inert sampling bags (e.g., Tedlar bags). Continuous methods include chemically based analyzers, such as chemiluminescence methods for ozone and NO_x , or spectroscopic methods.

Special measurement challenges encountered when using aircraft measurement platforms include 1) engineering design considerations, such as size, weight, and electrical consumption of the instrument, all of which must be minimized for sampling aboard aircraft platforms, and robustness to handle the excessive electrical and vibrational noise associated with the aircraft; 2) measurement considerations, such as the analytical sensitivity of the method, time resolution needed to meet study objectives, and effects of rapid changes in temperature, pressure, and relative humidity; and 3) aircraft design considerations, which pose special challenges, such as those associated with design and location of sample inlets and manifolds. Daum and Springston (1993) recently reviewed sampling considerations associated with the use of aircraft platforms

for obtaining gas- and particulate-phase measurements aloft, while McMurry (1998) highlighted considerations associated with sampling inlets and collection of particles and gases at high speeds. The discussion below summarizes important points from these reviews.

Sampling from a platform that can change altitude quickly requires either methods that are independent of changes in temperature, relative humidity, and pressure, or a methodology to correct for the effect of changes on these variables on the data collected. The largest concern comes from changes in pressure that result from changes in altitude. Sensors can be mass dependent or concentration dependent. True mass dependent sensors are independent of pressure, while concentration dependent sensors are dependent on pressure. However, it may not be obvious for the sampling-detection system as a whole, since one component of a system may be mass dependent, while another may be concentration dependent. An example of this situation is given by Daum and Springston (1993), who point out that the measurement of SO₂ by the flame photometric instrument has both mass and concentration dependent components.

Instrument response time is another critical factor when sampling aboard aircraft platforms. For example, aircraft used to collect pollutant data in the lower troposphere typically fly at speeds from 50 to 200 km/s. Therefore, a 10 s sample covers a spatial extent from 0.5 to 2 km, while for a one-hour sample the distance covered would range from 180-720 km. A one-hour averaged sample results in a spatial distance much greater than the grid size currently in use in Eulerian air quality models. Therefore, short integration times are desirable. There is however a trade-off between resolution, sensitivity, and noise. Shorter sampling times often result in more noise, poorer precision, and less sensitivity.

The sample inlet or probe and transfer tubes must be designed so that the composition of the ambient sample is not altered, chemically or physically. Sampling from a moving platform creates a particularly difficult challenge for the collection of particles, if the size distribution and phase equilibrium must be preserved. The size distribution can be altered if sampling is not conducted under isokinetic conditions, resulting in either positive or negative biases. Phase equilibrium can change due to compression heating of the gases as they are slowed and undergo adiabatic compression

in the collection tube. Both potential problems can be minimized by careful design of the sampling system. In general, collection of gases require the same considerations as sampling at ground level, with most concerns centered around the loss of reactive species on sampling inlets and transfer tubes. However, with aircraft, special consideration must be given to the condensation of water on transfer tubes, that may result in the potential for additional losses of gas-phase species. The sampling probe must extend outside the boundary layer of the aircraft and be free of the propeller-wash and pollutant emissions from engine exhaust and engine heaters.

When sampling from an aircraft, consideration must also be given to the payload and power capabilities of the aircraft. A small plane may be able to carry payloads only as large as 250 kg with very limited space available. Consequently, many ground-based methods have been modified to be smaller and lighter in weight. Aircraft also typically operate on 28 v DC and 400 Hz, while laboratory methods typically operate at 110 v or 220 v and 60 Hz. Therefore, special converters must be added to the aircraft or the instruments must be converted to 28 v.